LEAD CYCLING THROUGH A HAZARDOUS WASTE-IMPACTED WETLAND

BY

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To my lovely wife, Taipau

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This study investigated the fate of Pb at a heavily impacted wetland in Jackson

County, Florida. Several approaches involving different perspectives were initiated. From

a microscopic point of view, the stabilities of Pb complexed with humic substances in the

aquatic environment were studied to assess the potential of Pb remobilization. Meanwhile,

a macroscopic system analysis was conducted as well to evaluate the benefits of wetland

ecosystem restoration. Microcosms containing cypress (*Taxodium ascendens*) and black

gum (*Nyssa sylvatica*) seedlings were used as a wetland surrogate to assess the ecological

effects of Pb and acidity on the wetland community. Possible mechanisms of transport and

transformation of Pb in the wetland environment were postulated and tested.

Lead analyses of surface water, sediment, vegetation, and biota were conducted to

evaluate the biogeochemical cycling of Pb in a wetland ecosystem. Surface water showed

only trace amounts of Pb; i.e., less than 0.01 mg/L at most sites. A majority of Pb was

bound to the sediment, although decreasing concentrations were noticed in this

compartment between 1989 and 1992. High Pb levels in the below-ground biomass of

most aquatic species were found to be associated with Pb in the sediment. The bioconcentration factors (BCF) of aquatic species were determined. *Hypericum* sp. had the highest BCF (41) in the below-ground biomass.

The microcosms indicated that there were no significant effects ($\alpha=0.05$) on seedlings grown under simulated field pH and Pb conditions. A continuous-flow system employing equilibrium dialysis, which was first developed for this study, was used to measure conditional stability constants. The results indicated a decrease in Pb-complex stabilities from 5.34 to 5.10 as pH decreased from 7 to 3.

Three wetland management alternatives were proposed. These included land protection, sediment excavation, and wetland restoration by replanting. An "emergy"-based ecological-economic evaluation revealed that restoration of the wetland was the most beneficial option, with a net benefit of 15.1E+17 and 57.4E+17 solar emjoules (sej) for 20-year and 62-year recovery times, respectively. The net benefit of this alternative is calculated to be \$757,000 and \$2,870,000 for the 20-year and 62-year recovery periods, respectively, based on macroeconomic values for the U.S.economy in 1990, 2.0E+12 sej/\$.

1.1 Introduction

Wetlands are among the most important and least understood ecosystems on earth (Ewel and Odum, 1984; Mitsch and Gosselink, 1986). As early as the 14th century in Dante's *Divine Comedy*, wetlands was described as evil and forbidding places with little economic value. Prior to the mid-1970s, the value of wetlands was still not well recognized. Drainage and destruction of wetlands were accepted and practiced throughout the United States, and were even encouraged by certain government polices (Mitsch and Gosselink, 1986).

It was not until the 20th-century population expansion that wetlands became the focus of some conservation efforts because of their importance to water management, wildlife conservation, and many other functions. However, many of these benefits are still neither clearly understood nor wisely used. Understanding wetland ecosystems is a major goal of contemporary ecological science, and is a necessary prerequisite to land use management philosophies that will permit such ecosystems to serve as a harmonious interface between humanity and nature (Ewel and Odum, 1984).

1.2 Background

The Steel City Bay wetlands in Jackson County of western Florida were heavily impacted by inputs of acidic battery wastewater discharge from Sapp Battery Service, Inc. from 1970 to 1980. Wetland structures and functions were altered by the associated ecotoxicity effects. Devastation of the wetland community was observed with respect to the predominant species, pond cypress (*Taxodium ascendens*) and black gum (*Nyssa*

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sylvatica). Even though more than a decade has passed subsequently, the residuals of acid and Pb in wetland sediments at this site still strongly influence proper functioning of the wetland ecosystem.

Low pH values for surface waters were commonly reported on-site, off-site, and even in downstream wetlands. Elevated Pb concentrations in sediments also were reported (CH$_2$M HILL, Inc., 1991; Ecology and Environment, Inc., 1986; Mundrink, 1989; Ton, 1990; Ton et al., 1993; Trnovsky et al., 1988). The vertical profiles of sediment indicated that Pb had accumulated in the top layers of sediment (0-15 cm). However, the concentration of Pb in surface waters decreased dramatically after the battery service plant ceased operation. Results from sequential chemical extractions revealed that organically bound Pb was the predominant form of Pb in these sediments (Ton, 1990; Ton et al., 1993).

1.3 Objectives of this Study

The basic objective of this study is to understand the fate of Pb in a wetland ecosystem. Field studies, microcosm studies, laboratory studies, and "emergy"-based ecological-economic evaluations are all included in the study. The field studies are intended to collect information on Pb transport and transformations. The distribution of Pb in the wetland ecosystem can then be used to determine approaches for the remaining tasks. Due to the principles of biogeochemistry, materials tend to be retained in compartments with longer residence times, e.g., organic-rich sediments and vegetation. Laboratory studies, therefore, are helpful to assist in characterizing the stability of Pb in the sediment under different environmental conditions; i.e., at varying pH values and redox potentials. Microcosms, representing simplified ecosystems though still having a level of complexity, are often used for ecotoxicity assessments. Field conditions were matched as closely as possible in the microcosms. The "self-organization" of microcosms was also pursued to mimic the natural ecosystems under limitations of the available experimental design.

The objectives of this study are summarized as follows:

1. to obtain an overview of the fate of Pb through a heavily impacted natural wetland ecosystem,

2. to evaluate the effects of acidity and Pb concentration on the growth of wetland species,

3. to evaluate the stabilities of organo-Pb complexes under different environmental conditions,

4. to improve the experimental technique for the determination of organo-Pb stability constants, and

5. to provide an alternative approach to wetland management through use of an ecological-economic evaluation method based on the aforementioned studies.

1.4 Organization of the Dissertation

This dissertation is divided into five chapters. Chapter 1 presents the introduction, background, objectives, and organization of the dissertation. Chapter 2 cover a literature review of wetlands; microcosms; ecotoxicologies of acidity and heavy metals; Pb contamination and complexation of Pb with humic substances; heavy metal movement, distribution, and availability; rehabilitating damaged ecosystems; and system analysis.

Chapter 3 describes the area investigated, sampling procedures, and analytical methods. Devastation of the wetland community provides strong evidence of ecotoxicity. Water chemistry data, and samples of surface water, sediment, and vegetation were collected periodically from the Steel City Bay wetlands from April 1989 to September 1992. Eleven sampling sites were selected for the study, including one field control site. Total Pb analyses were conducted for each sample. Bioconcentration factors for different vegetation also were determined. The bioconcentration factor is an indicator of metal tolerance by plants, and also of plant participation in the biogeochemical cycle. Humic substances were isolated from surface water collected at the control site.

A newly developed method of dialysis analysis was employed for the determination of the conditional stability constants of organo-Pb complexes. Microcosms were established to investigate Pb toxicity and acid tolerance during seedling growth in order to facilitate decisions regarding revegetation efforts. Systems analysis was used to study the complexity of the interactions between human activities and the natural environment.

Results and discussion of the field, microcosm, and laboratory studies, and ecological-economic evaluations of alternative strategies for wetland management are included in Chapter 4. The field study suggested a gradual recovery of the damaged wetland ecosystem. The microcosm studies showed that there are no significant effects on seedling growth under simulated field conditions. The laboratory studies indicated that the Pb binding capacities of humic substances and the conditional stability constants of organic-Pb complexes corresponded with pH. A macroscopic view of wetland management then served to combine the above efforts. An ecological-economic method was used to evaluate three alternative strategies of wetland management proposed herein. The alternative requiring less input of energy and resources, but having the highest societal benefit was identified.

Chapter 5 presents the summary and conclusions for this research.

CHAPTER 2
LITERATURE REVIEW

2.1 Wetlands

Wetlands are known as transition zones, or ecotones, from uplands to deepwater aquatic systems. This transitional position allows wetlands to serve as organic matter exporters and as inorganic nutrient sinks. On a short time scale, "wetlands are valuable as sources, sinks, and transformers of a multitude of chemical, biological, and genetic materials" (Mitsch and Gosselink, 1986). Nixon and Lee (1986) have postulated that wetland systems might act in differing ways at different times of the year. Therefore, wetlands have been described as "the kidneys of the landscape" due to the functions they perform in hydrologic and chemical cycles and as downstream receivers of wastes from both natural sources and humans (Mitsch and Gosselink, 1986)

Wetlands also are recognized as providing many services of importance to wildlife and humans, including aquifer recharge, recreational opportunities, habitats for animal and waterfowl, stormwater and flood control, timber and vegetation harvest, and water quality maintenance (Carter, 1986; Mitsch and Gosselink, 1986; Sather and Smith, 1984; U.S. Army Corps of Engineers, 1972; Williams and Dodd, 1979).

Although wetlands have a number of characteristics that distinguish them from other ecosystems, their delineation remains controversial. The difficulties in defining wetlands are due not only their great geographical extent, but also to the wide variety of hydrological conditions in which they are found. Some definitions developed by several federal agencies are given in Table 2-1. Among the distinguishing features of wetlands, the most notable are the periodic presence of standing water, and the presence of unique

Table 2-1. Definitions of wetlands.

1 "A tract of land having wet and spongy soil, as a marsh, swamp, or bog."
  Source: Webster's Encyclopedia Dictionary (1989).

2 "Wetland is defined as land having the water table at, near, or above the land surface
  or which is saturated for a long enough period to promote wetland or aquatic
  processes as indicated by hydric soils, hydrophylic vegetation, and various kinds
  of biological activity which are adapted to the wet environment."
  *Source: Tarnocai, 1979. Canadian Wetland Registry.

3 "Wetlands are lands transitional between terrestrial and aquatic systems where the water
  table is usually at or near the surface or the land is covered by shallow water ..."
  "... Wetlands must have one or more of the following three attributes: (1) at least
  periodically, the land supports predominantly hydrophytes, (2) the substrate is
  predominantly undrained hydric soil, and/or (3) the substrate is nonsoil and is saturated
  with water or covered by shallow water at some time during the growing season of
  each year."
  *Source: Cowardin et al., 1979. U. S. Fish and Wildlife Service.

4 "Wetlands mean those areas that are inundated or saturated by surface or ground
  water at a frequency and duration sufficient to support, and that under normal
  circumstances do support, a prevalence of vegetation typically adapted for life
  in saturated soil conditions..."
  *Source: U. S. Army Crops of Engineers (1984).

* Sources cited from Mitsch and Gosselink, 1986.

wetland soils, and/or of vegetation adapted to or tolerant of saturated soil sources (Mitsch and Gosselink, 1986).

Recently, scientists have become increasingly interested in the capability for improving water quality by removing organic and inorganic nutrients and toxic materials from surface waters through the use of natural and constructed wetlands.

Three possible pathways for the transport and transformation of organic and inorganic pollutants applied to wetland ecosystems may be expected:

1. uptake by plants,

2. movement to groundwater or surface water, and

3. immobilization in the soil matrix (Chan et al., 1982).

Best et al. (1982) reported an 80-90% decrease in the concentration of soluble metals within 40 m for a forest wetland near Waldo, Florida. Interactions of heavy metals with naturally occurring organics were believed to be the major factor that controlled metal immobilization in their study. In another review of wastewater application to wetlands, Best (1987) indicated again that wetlands were efficient in removing heavy metals as well as nutrients from any associated water column. The data also suggested that wetlands may be used for enhancing water quality and for recycling wastewater without adversely affecting wetland ecosystems.

In a constructed wetland wastewater-treatment system in Idaho Springs, Colorado, low pH and high concentrations of heavy metals in mine drainage were treated (Judith et al., 1991). The passive treatment technology in this pilot study relied on artificial wetlands to promote biogeochemical mechanisms, thereby raising the pH of mine drainage and removing metals. Results indicated an increase in water pH from 5.6 to 7.7 and from 2.5 to 7.4 at two different sites. Metals removal was over 95% to 99% for different metallic elements. Various removal mechanisms for pollutants in wetlands and aquatic systems are listed in Table 2-2 (Chan et al., 1982). Apparently, heavy metals can be effectively retained by either physical or chemical removal mechanisms.

Table 2-2. Physical and chemical pollutant-removal mechanisms in wetland and aquatic systems.

Mechanism	Settleable solids	Colloidal solids	Organic compounds	Petroleum hydrocarbons	Nitrogen	Phosphorus	Heavy metals	Bacteria & viruses	Halogenated hydrocarbons	Description
				Pollutant affected						
Physical										
Evaporation			X	X			X*		X	Volatilization and aerosol formation
Sedimentation	X	X		X	X	X	X**		X	Gravitational settling of particles and adsorbed pollutants
Emulsification		X	X	X			X*		X	Suspension of chemicals that are sparingly soluble in water within an aqueous environment
Adsorption		X	X	X			X	X	X	Electrostatic attraction, Van der Waals forces
Filtration	X	X						X		Mechanical filtration of particles through substrate, root or animal systems
Chemical										
Chelation						X	X			Formation of metal complexes through ligands
Precipitation				X		X	X			Formation or co-precipitation of insoluble compounds
Decomposition			X	X			X	X	X	Alteration of less-stable compounds by oxidation, reduction, hydrolysis or photochemical reactions
Chemical adsorption			X	X	X	X	X		X	Covalent bonding, hydrogen-bond formation, hydrophobic interactions

* Significant only for mercury.
** Not significant for manganese and mercury.
(Adapted from Chan et al., 1982)

The National Aeronautics and Space Administration (NASA) research center in southern Mississippi has conducted research for many years into the use of aquatic plants for treating and recycling domestic wastewaters, including heavy metals removal. The scientists have observed that several vascular aquatic plant species, such as water hyacinth (*Eichhornia crassipes*), torpedo grass (*Panicum repens*), and Southern bullrush (*Scirpus californicus*), are capable of improving water quality in many ways (Wolverton and Bounds, 1988; Wolverton and McDonald, 1977, 1978). Dierberg and Brezonik (1984) also reported a high percentage of nutrient removal from surface water during wastewater discharge to a cypress swamp. The nutrients were retained and taken up by tree species in the cypress domes.

A more comprehensive study of the use of wetlands for water pollution control by Chan et al. (1982) revealed the effectiveness of wetlands for water quality improvement. Some systems (see Table 2-3) evidenced a high removal efficiency for nutrients (90-99%) and Pb (60-96%).

2.2 Microcosms

Pritchard and Bourquin (1984) defined microcosm studies as "an attempt to bring an intact, minimally disturbed piece of an ecosystem into the laboratory for study in its natural state". Theoretically, the microcosm is a simplified natural ecosystem that maintains a level of complexity. Within definable physical and chemical boundaries and under a standard set of experimental conditions, the microcosm system, whether derived from natural communities or synthesized from laboratory cultures, is considered an analog of the field. In other words, studies with microcosms can serve as surrogates for actual field studies (Beyers and Odum, 1992; Pritchard and Bourquin , 1984).

Early ecologists tended to refer to microcosms as synonymous with ecosystems. In modern ecology, a microcosm is taken to mean a small experimental ecosystem.

Table 2-3. The effectiveness of wetlands in water quality improvement.

System/location	Wetland type	Hydrologic factors	Application concentration	Removal efficiency	Comments and reference
Clermont, Florida (1)	Freshwater marsh	Four 200 m² plots Loading rate of 1.3, 3.8, or 10.2 cm/wk	Total N of 1.14 kg/(ha)(d)

Total P of 1.19 kg/(ha)(d) | 97.3%

97.5% | Dead standing crop and below-ground biomass acted as N sinks.

Storage in roots, litter and the soil complex accounted for P reduction. (Zoltek et al., 1978)* |
| Wildwood, Florida (1) | Hardwood swamp | 202 ha swamp area 672 ha watershed 570 m³/d wastewater input | Total N of 15.3 mg/L

Total P of 6.4 mg/L

Wastewater
Pb   0.03 mg/L
Urban runoff
Pb   0.02 mg/L | 89.5%

98.1% - seasonal 13% - annual

(Average reduction for combined wastewater and urban-runoff flow) 60.0% | High level of N-removal during the growing season (Aug - Sept) due to plant utilization.

P release during the dormant period lowered the annual removal efficiency.

No study of uptake and removal mechanisms. (Boyt et al., 1977)* |
| Montgomery, Maryland (2) | Wetland detention basin | 60 ha watershed 2.4 ha permanent pond with 45,600 m³ dead storage capacity Depth - 0.9 - 4 m 22 hr. detention time peak inflow 0.62 m³/s | Ammonia-N   3 g/s

Total P   0.3 g/s

Pb   0.18 mg/s | 99%

99%

96% | Large permanent pond volume is the key factor in high pollutant-removal efficiency (Lynard et al., 1980; McCuen, 1978)* |

(1) Wetland-wastewater treatment system   (2) Wetland-stormwater treatment system
* Reference cited from Chan et al., 1982

Microcosms have been utilized repeatedly in environmental risk-analysis, including the fate of chemical pollutants (Harper, 1985; Owens and Best, 1989; Tuschall, 1981) and the assessment of pollution effects (Jenner and Bowmer, 1990; Samant et al., 1990; Scanferlato and Cairns, 1990; Wolverton and McDonald, 1978).

Microcosms also are recommended for assessing ecosystem-level effects of toxic chemicals. While most chemically-induced alterations of properties such as toxicity effects and biogeochemical cycling could be done most realistically on intact natural ecosystems, it is not generally economically nor logistically feasible to do large-scale field testing. Leffler (1984) considered microcosms as "small living models of ecosystem processes". They offer the advantage of short time scales, small physical size, replicability, reproducibility, and no associated contamination of the natural environment. They are also relatively inexpensive to use, and may be standardized to produce qualitative predictions regarding potential environmental impacts (Beyers and Odum, 1992; Leffler, 1984).

Both quantitative and qualitative assessments are commonly used in environmental-risk analysis (Pritchard and Bourquin, 1984). Qualitative assessments establish risk by comparing test information (fate or effects) against previously tested data using a standardized test method. Quantitative assessments are synonymous with determination of waste assimilative capacity. From a quantitative standpoint, to characterize the waste assimilative capacity of any particular environment is to assess the potential of that environment to accept a certain level of pollution without adverse effects.

The use of microcosms to assess environmental impacts is still controversial. Scientists have considerable and continuing interest in the ability of microcosm results to predict natural ecosystem responses. In the meantime, scientists have been conservative in their claims of what such research might accomplish (Taub, 1984), being aware of the inherent restrictions and limitations of microcosms. However, microcosms have generally been designed to answer different types of questions that can be well addressed by the

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system used. Therefore, suitability of the use of microcosms to interpret natural responses must depend on the questions being asked.

2.3 Ecotoxicology of Acidity and Heavy Metals

The term "ecotoxicology" was first introduced in the late 1960s by Truhaut to describe the ever-increasing amounts of pollution in natural environments (Boudou and Ribeyre, 1989). It is concerned with the toxic effects of chemical and physical agents on living organisms, and especially on populations and communities within defined ecosystems. The main aims of ecotoxicology are the analysis of transfer processes for contaminants within natural systems and study of the structural and functional effects to which they give rise.

In general, plants grow at optimum rates under near-neutral soil pH conditions (Bohn et al., 1985; Grunwald et al., 1988). Elevated hydrogen-ion concentrations in the soil solution are generally caused by active oxidation of nitrogen, sulfides or organic sulfur compounds. When reduced sulfur is oxidized (naturally and/or microbially) to H_2SO_4, the resultant acidity can be reflected in pH as low as 1.5 to 2 (Bohn et al., 1985).

Soil pH can have both direct and indirect effects on plants. Direct effects occur at relatively low soil pH, namely, less than pH 4. Soil acidity also can cause an increase in exchangeable aluminum ions to toxic levels in the soil solution, however, which restricts or even stops the growth of roots (Bohn et al., 1985). Elevated H^+ concentrations also can cause a decrease in the availability of many nutrients, including P, K, Mg, Ca, and Mo (Grunwald et al., 1988). Indirect effects of soil acidity commonly include increased availability of heavy metals and increased infection by some soil pathogens (Grunwald et al., 1988; Guyette et al., 1991).

The potential ecotoxicity of metal-polluted soil usually is monitored by chemical analysis, plant community composition, and the survival and growth of soil/sediment organisms (Fletcher, 1990; Seaward and Richardson, 1990). Vegetation usually is among

the first interceptors of acidity and heavy metals deposited to an ecosystem. If an ecosystem is sparsely vegetated, soils may be an early interceptor of such deposits as well (Friedland, 1990).

When plants accumulate toxic amounts of metals such as Cu, Cd, Pb, or Zn, the activity of some enzymes may increase in leaves and/or in roots. Such enzyme induction is strongly correlated with the inhibition of shoot growth. Stunted growth, leaf elongation, and chlorosis are visible symptoms of strong phytotoxicity from metals. At lower degrees of pollution, reduced plant quality and biomass production are common (Assche and Clijsters, 1990).

In a study of several mine sites, high concentrations of Cu, Cd, Pb, and Zn along with low pH in mine drainage waters proved very common (Judith et al., 1991). Thus, the mine sites were sparsely vegetated, the trees often small and stunted, and some appeared chlorotic or necrotic (Nriagu, 1978b; Wickland, 1990).

In a study of the molecular mechanisms of metal-ion toxicity with respect to plant growth, Ochiai (1987) pointed out that such mechanisms can be divided into five general groups:

1. displacing essential metal ions from biomolecules and other biologically functionally units;

2. blocking essential functional groups of biomolecules, including enzymes and polynucleotides;

3. modifying the active conformation of biomolecules, especially enzymes and polynucleotides;

4. disrupting the integrity of biomolecules; and

5. modifying some other biologically active agent.

The basis for these mechanisms, especially the first three, is the ability of metal ions to bind strongly to oxygen, nitrogen, and sulfur atoms. These atoms are abundant in biological systems and can serve as ligands to all essential metal ions. In many cases, the metal ion at the active site can be displaced by a different metal ion, forming a derivative

with altered biological activity. In addition, toxic metal ions can coordinate to essential functional groups of proteins, rendering the protein inactive (Borovik, 1990).

Seaward and Richardson (1990) mentioned that plant roots can take up metal ions from contaminated soil, though considerable amounts are generally bound to the walls of root cells. Even metal ions transported through the xylem tend to be adsorbed onto the walls of the vessels, resulting in changes in cation concentrations of the fluid. Higher metal levels occur in roots from acid soils, and inhibitory effects on mycorrhizae may partially account for decreased plant growth in areas subject to acid deposition and/or the presence of toxic metals. A summary of some major constraints of acidity and heavy metals on plant growth appears in Table 2-4 (Assche and Clijsters, 1990; Bohn et al., 1985; Macnair, 1990; Marschner, 1991; Wu, 1990).

In a review of the toxicity of metals in culture solution, McNeilly (1987) indicated that the metals primarily affect root growth. Concentrations of 12 μg Pb/g (dry weight) typically cause total root-growth inhibition. Påhlsson (1989) also reported that comparatively low levels of Pb in the soil solution, ranging from 5 to 50 μg Pb/g, affect the growth of vascular plants. Such effects vary among plant species. However, in most studies, only high levels of Pb in the growth medium have proved to affect the growth of plants (Adriano, 1986; Påhlsson, 1989; Peterson, 1978).

In nutrient solutions containing ca. 400 μg Pb/L as the chloride, a 50% decrease in root elongation by *Picea abies* seedlings was observed. A five times higher Pb level also was reported to influence root growth of *Agrostis capillaris* . Thus, it is believed that the phytotoxicity of Pb is relatively low compared with other trace elements (Adriano, 1986; Påhlsson, 1989).

Like other heavy metals, Pb also is only slightly toxic to seed germination. Concentrations as high as 20,000 μg Pb/L in the medium did not affect seed germination of four tree species, nor was pH found to interfere (Påhlsson, 1989). Nevertheless, such

Table 2-4. Major constraints of acidity and heavy metals on plant growth.

Acidity (pH ≤ 3.0)			Metals		
Factor	Result	Ref.	Factor	Result	Ref.
Increase in H⁺ concentration	H⁺ toxicity	1, 2	Leaf elogation	Biomass reduction	3
Increase in Al concentration	Al toxicity	1,2	Leaf chlorosis	Plant quality reduction	3
Increase in Mn concentration	Mn toxicity	1,2	Metal tolerance	Slower growth rates	4
Decrease in other metal cation concentrations	Mg, Ca, K deficiency	1	Metal tolerance	Lower biomass production	4
Inhibition in metal cation uptake	Mg, Ca, K deficiency	1	Enzyme increase in roots	Inhibition of root growth	3, 5
Decrease in P and Mo solubility	P, Mo deficiency	1,2	Enzyme increase in leaves	Inhibition of shoot growth	3
Inhibition of root growth	Nutrient and water deficiency	1,2			
Increase in leaching	Nutrient deficiencies	1			

References cited from: 1— Marschner, 1991;   2— Bohn et al., 1985;   3— Assche and Clijsters, 1990;
4— Wu, 1990; 5— Macnair, 1990.

results may not be useful for interpretation of probable plant growth without information concerning further development of radicles and hypocotyls.

Lead ions also are shown to inhibit chlorophyll biosynthesis, leading to lowered chlorophyll contents in leaves, and thus inhibiting photosynthesis (Adriano, 1986; Påhlsson, 1989). Low concentrations of Pb, however, may instead result in stimulation effects. Studies have shown that the net photosynthesis of *Medicago sativa* actually increased when exposed to 100 μg Pb/L, and a decreased rate was observed only at 100,000 μg Pb/L (Påhlsson, 1989). Another study indicated that a rooting-media concentration of Pb, as the nitrate, of 25,000 μg Pb/L was required to cause toxicity. At a concentration of 50,000 μg Pb/L, plant death occurred (Adriano, 1986).

In other studies, higher plants were absent from soils with the highest concentrations of Pb, i.e. up to 24,500 μg/g (Peterson, 1978), but total Pb concentrations of only 400 to 500 μg/g in the soil of a polluted area in Japan were found to be toxic to plants (Adriano, 1986). Therefore, Pb toxicity generally varies among species and is also associated with chemical forms of Pb.

Sediment criteria for Pb also have been proposed by several state and federal agencies to evaluate potential toxicity to aquatic plants and biota. A summary of these proposed sediment-quality criteria, guidelines, and toxic-effect values for Pb is given in Table 2-5 (Bonnevie et al., 1992).

2.4 Lead Contamination and Complexation of Pb with Humic Substances

2.4.1 Origins of Pb Contamination

Lead is not uniformly distributed in the earth's crust. Through the effects of natural processes (erosion, weathering) and human activity (mining), Pb is made available to the environment.

Table 2-5. Summary of proposed sediment-quality criteria, guidelines, and toxic-effect values for lead.

Criteria and guidelines	Proposed concentration	Reference*
	(µg/g)	
Washington State Department of Ecology Marine Sediment Criteria (1991)	450	WADOE, 1991
California State Water Resources Control Board Amphipod Bioassay AET Value (1990)	340	CSWRCB, 1990
Ontario Ministry of the Environment Severe Effects Level	250	Persuad, 1991
California State Water Resources Control Board Bethnic Evaluation AET Value (1990)	150	CSWRCB, 1990
United States Environmental Protection Agency Threshold Value (1985)	132	USEPA, 1985
National Oceanic and Atmospheric Administration Effect Range - Median (1990)	110	NOAA, 1991
California State Water Resources Control Board Bivalve Larvae Bioassay AET Value (1990)	71	CSWRCB, 1990

* References cited from Bonnevie et al., 1992
AET - Apparent Effects Threshold.

Lead has been known to mankind since about 2500 B.C, with metallic Pb and its compounds being used extensively for the last 4000 years. Metallic Pb has been used in the manufacture of pipes, cisterns, and anticorrosion containers, and in alloys with antimony, tin, and copper for the manufacture of accumulator plates in storage batteries. Lead compounds also have been important in the pottery industry, including such uses as pigments in paints, prints, and varnishes Some Pb compounds also have been used in the manufacture of insecticides and plastics (Venugopal and Luckey, 1978).

Several studies have indicated that the most significant source of Pb in our environment in recent years has been that generated by industrial processes, rather than natural deposition or domestic wastewater discharge (Hellawell, 1988; Nriagu, 1988; Trnovsky et al., 1988).

Hellawell (1988) indicated that the principal sources of Pb in the environment are the use of leaded gasoline and contributions from batteries and paint. It was reported that nearly 80% of the Pb consumed in the United States in 1989 was destined for use in storage batteries (Gruber, 1991). Venugopal and Luckey (1978) also estimated that over five million tons of Pb were used from 1920 to 1970 in the Northern Hemisphere in automobile fuel in the form of tetraethyl Pb.

The combustion of Pb-containing fuels has been reported to be the primary source of Pb in the atmosphere, resulting in a release of 61% of the Pb of anthropogenic origin into the environment during the 1970s (Nriagu, 1978a). Industrial emissions, fossil-fuel combustion, and vehicular emissions contributed most of the airborne Pb (Harrison and Laxen, 1981). However, the gradual removal of Pb from gasoline during the 1980s may decrease this figure somewhat in future years (Harper, 1985).

2.4.2 Lead Transport and Transformations during the Hydrocycle

The processes and global patterns for the circulation of heavy metals in ecosystems are still evolving with respect to understanding the relationships between heavy metals and various compartments of the ecosystem. Elemental movement generally is referred to using three terms: inputs, outputs, and fluxes through the system. There are also three major sources of Pb for each ecosystem: the underlying parent material, the atmosphere, and the aquatic environment (Salomons and Förstner, 1984).

Lead in water is originally obtained from one of the other two sources. Particulates and gases from volcanoes, forest fires, crustal material, and continental dust always have provided natural inputs of Pb to soils and ecosystems (Friedland, 1990). On a global basis, calculations of mining production, emission rates to the atmosphere by human activities, atmospheric precipitation, and stream fluxes of metals may be used to estimate the human contributions to metal contamination (Garrels et al., 1975).

A summary from previous studies of Pb concentrations in environmental reservoirs, along with associated fluxes, is given in Table 2-6 (Chester, 1990; Davies, 1990; Garrels et al., 1975; Harrison and Laxen, 1981; Salomons and Förstner, 1984; Schlesinger, 1991).

Since the residual levels as well as the turnover time of Pb in the atmosphere are small, the atmosphere serves as an important medium of transfer rather than as the major source pool for Pb. Lead and other trace metals have been transported along the hydrological cycle since the first occurrence of water on the earth. Water provides both the medium for weathering of the continents and the medium for transport of trace metals (Salomons and Förstner, 1984).

Figure 2-1 gives a schematic presentation of the movement of trace metals during the hydrological cycle. Along the pathway from continents to oceans, Pb is subject to a large number of processes. During transport, environmental changes affect the distribution

Table 2-6. Summary table for storages and fluxes of Pb in the biogeochemical cycle of the earth.

Items	Type	Unit	Reference	*
Reservoirs (concentration)				
Continents	Rock	1.60E+01 µg/g	Martin and Witfield, 1983	1
		2.23E+01 µg/g	Wedepohl, 1972, 1974	5
	Sedimentary	2.30E+01 µg/g	Davies, 1990	2
	Igneous	1.80E+01 µg/g	Davies, 1990	2
	Mean crust	1.60E+01 µg/g	Davies, 1990	2
	Soil	3.50E+01 µg/g	Martin and Witfield, 1983	1
		2.92E+01 µg/g	Ure and Berrow, 1982	5
		4.20E+01 µg/g	Davies, 1990	2
	Sediment	3.40E+01 µg/g	Forstner, 1978	5
	Mean sediment	1.90E+01 µg/g	Bowen, 1979	5
		1.60E+01 µg/g	Garrels et al., 1975	3
	Biomass	2.00E+00 µg/g	Garrels et al., 1975	3
Rivers	Dissolved	1.00E-01 µg/L	Martin and Witfield, 1983	1
		2.00E-01 µg/L	Trefry and Presley, 1976	5
	Particulate	1.00E+02 µg/g	Martin and Witfield, 1983	1
		1.50E+02 µg/g	Martin and Meybeck, 1979	5
Ocean	Dissolved	3.00E-03 µg/L	Martin and Witfield, 1983	1
		3.00E-02 µg/L	Garrels et al., 1975	3
	Subsurface	1.00E-03 µg/L	Crecelius, 1982	5
	Deep sea clays	2.00E+02 µg/g	Martin and Witfield, 1983	1
Atmosphere	Aerosol	3.00E-03 µg/kg**	Garrels et al., 1975	3
	Rural	3.60E-03 µg/kg	Cawse, 1981	5
	Urban	3.40E-01 µg/kg	Cawse, 1981	5
	Marine	4.08E-02 µg/kg	Schlesinger, 1991	6
Fluxes				
Land — Air	Continental dust	1.60E+10 g/yr	Nriagu, 1979	5
		5.00E+09 g/yr	Lantzy and MacKenzie, 1979	6
		3.00E+09 g/yr	Weisel et al., 1984	1
	Volcanogenic dust	6.40E+09 g/yr	Nriagu, 1979	5
		8.70E+08 g/yr	Lantzy and MacKenzie, 1979	6
		4.00E+08 g/yr	Weisel et al., 1984	1
	Volcanogenic gas	1.20E+06 g/yr	Lantzy and MacKenzie, 1979	6
	Forest fire	5.00E+08 g/yr	Nriagu, 1979	5
	Vegetation	1.60E+09 g/yr	Nriagu, 1979	5
		2.00E+08 g/yr	Weisel et al., 1984	1
	Leaded gasoline	2.92E+11 g/yr	Harrison and Laxen, 1981	3
	Fossil fuel	4.30E+11 g/yr	Lantzy and MacKenzie, 1979	6
		4.00E+09 g/yr	Weisel et al., 1984	1
		3.60E+09 g/yr	Bertine and Goldberg, 1971	5
		3.60E+09 g/yr	Garrels et al., 1975	3
	Industrial particles	1.60E+12 g/yr	Lantzy and MacKenzie, 1979	6
		4.49E+11 g/yr	Nriagu, 1979	5

Table 2-6. Continued.

Land — Ocean	River—(Diss.+Solid)	2.30E+12 g/yr	Martin and Meybeck, 1979	6
		1.25E+11 g/yr	Turekian, 1971	5
	Particulate	1.55E+12 g/yr	Martin and Witfield, 1983	1
		2.88E+11 g/yr	Garrels et al., 1975	3
	Dissolved	1.28E+11 g/yr	Garrels et al., 1975	3
		3.70E+09 g/yr	Schlesinger, 1991	6
Ocean — Air	Ocean emission	8.00E+09 g/yr	Weisel et al., 1984	1
	Sea spray	5.00E+09 g/yr	Weisel, 1981	5
Air — Land	Dry + wet deposition	1.50E+11 g/yr	Garrels et al., 1975	3
Air — Ocean	Dry + wet deposition	2.50E+11 g/yr	Garrels et al., 1975	3
Human activity	Mining production	3.10E+12 g/yr	Garrels et al., 1975	3
		3.00E+12 g/yr	Martin and Meybeck, 1979	5
Geological activity	Weathering	4.00E+11 g/yr	Garrels et al., 1975	3
	Sedimentation	5.00E+11 g/yr	Garrels et al., 1975	3

* References cited from: 1- Chester, 1990; 2- Davies, 1990; 3- Garrels et al., 1975;
    4- Harrison and Laxen, 1981; 5- Salomons and Forstner, 1984; 6- Schlesinger, 1991.
** 1 m^3 air at 15°C, and 760 mmHg = 1.226 kg
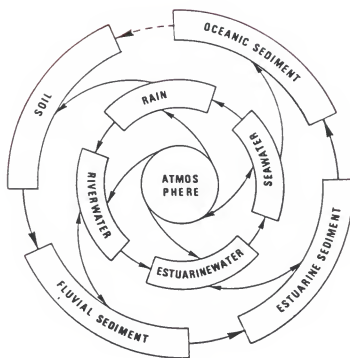
Figure 2-1. Movement of trace metals during the hydrological cycle.
(After Salomons and Förstner, 1984)

over the dissolved and particulate phases of Pb. Between suspended matter and the metals in solution, adsorption/desorption and (co-)precipitation processes take place (Harvey and Leckie, 1985; Lion et al., 1982; Rea et al., 1991; Salomons and Förstner, 1984; Sheppard and Thibault, 1992).

The accumulation of particulate Pb causes a reduction in transport to the oceans which, under normal conditions, takes only days or weeks. The suspended matter and the deposited sediments are interlinked through sedimentation and erosion processes, which may temporarily accumulate particulate Pb and other metals in lakes and rivers or in other systems, including wetlands.

However, this does not mean that those metals are *removed* from the system. Sediments act merely as a reservoir, and changing environmental conditions may cause a remobilization of the accumulated metals. Processes taking place after deposition (diagenesis) provide the interstitial waters with at-times-high concentrations of trace metals which, through processes such as diffusion and consolidation, are able to influence the metal concentrations of surface waters. All the reservoirs in aquatic systems, and groundwater and the soil in the terrestrial environment, can influence metal uptake by biota (Salomons and Förstner, 1984).

2.4.3 The Nature of Humic Substances

Humus is a dynamic system which continually changes as its constituents decompose. The diverse processes which are involved are influenced by the physical, chemical, and biological conditions of the soil, and by human activity (Flaig, 1973). Thus, humic substances comprise a general class of biogenic, refractory, yellow-black organic substances that are widely distributed in soils, natural waters, marine and lake sediments, peat, and miscellaneous other deposits (Aiken et al., 1985; Stevenson, 1985).

Humic substances do not correspond to a unique chemical entity and, accordingly, cannot be described in unambiguous structural terms. Similarly, humic substances are not

biologically predestined to carry out a specific biochemical action and thus cannot be defined in strictly functional terms. As a result, neither a satisfactory characterization nor a consensus structure of humic substances ever exists (Aiken et al., 1985; Tuschall, 1981).

Despite the complexity and uncertainty of humic substances, several hypothetical structures have been proposed (Stevenson, 1982, 1985). Such structures consist mainly of complex hydrophilic polyelectrolytic units of benzene rings that are variously substituted with phenolic, carboxylic, or methoxy groups, together with large amounts of aliphatic carboxylic acids (Stevenson, 1982, 1985; Tuschall, 1981). Some hypothetical structures of humic substances are illustrated in Figure 2-2.

Humic substances can be operationally defined into three major fractions, according to their solubility in selected solvents. These fractions are obtained following alkaline extraction of the soil, and are as follows:

fulvic acid   soluble both in strong alkali and in strong acid;

humic acid   soluble in strong alkali but insoluble in strong acid; and

humin   insoluble both in strong alkali and in strong acid.

Although this fractionation scheme is arbitrary and the resultant fractions are molecularly heterogeneous, Schnitzer and Khan (1972) reported some properties that distinguish fulvic and humic acids. Fulvic acid tends to have lower color, carbon content, and molecular weight, and higher CEC (cation exchange capacity), oxygen content, and density of functional groups than does humic acid. Eventually, due to the more-soluble nature of fulvic acid, the humic substances in natural water reflect primarily the fulvic-acid fraction. Based on their elemental compositions and their oxygen-containing functional groups, a comparison between humic and fulvic acids is shown in Table 2-7.

Molecular weight is another important criterion for defining humic substances as well. Humic acids have a reported average molecular weight which ranges from 3000 to 1,000,000, and fulvic acids from 500 to 5000 (Stevenson, 1982). However, molecular
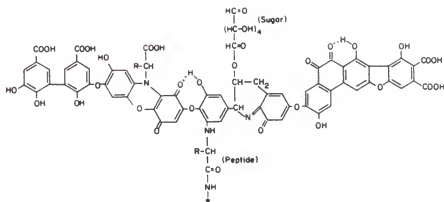
(a)
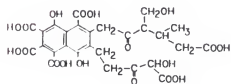
(b)

Figure 2-2. Some proposed structures of natural organic matter.
(a). Hypothetical structure of humic acid (After Stevenson, 1982)
(b). Proposed structure of fulvic acid (Adapted from Stevenson, 1985)

Table 2-7. The elemental composition and oxygen-containing functional groups in typical
humic and fulvic acids of soils.

Item	Humic Acids	Fulvic Acids
Elemental composition*	(%)	
Carbon—C	53.8—58.7	40.7—50.6
Hydrogen—H	3.2—6.2	3.8—7.0
Oxygen—O	32.8—38.3	39.7—49.8
Nitrogen—N	0.8—4.3	0.9—3.3
Sulfur—S	0.1—1.5	0.1—3.6
Functional group**	(meq/100g)	
Total acidity	560—890	640—1420
COOH	150—570	520—1120
Acidic OH	210—570	30—570
Weakly acidic + alcoholic OH	20—490	260—950
Quinone + ketonic C=O	10—560	120—420
OCH_3	30—80	30—120

* Source: Steelink, 1985.
** Source: Stevenson, 1985.

weight measurements on humic substances are highly dependent on pH, soluble-organics concentration, ionic strength, and other aspects of the method used (Steelink, 1985).

2.4.4 The Complexation of Pb by Humic Substances

Rickard and Nriagu (1978) described the chemistry of lead in soils as controlled by three processes:

1. adsorption at the soil mineral interface,

2. formation of relatively stable organo-lead complexes and insoluble organo-lead particulates and chelates, and

3. precipitation of relatively insoluble lead compounds.

The relative importance of these three controlling factors varies depending on the type of ecosystem, and ultimately determines bioavailability of the element.

Many authors have theorized that, in areas with abundant quantities of organic matter, most of the Pb is organically bound with there remaining relatively little "free" Pb (Garlaschi et al., 1985; Rudd et al., 1988; Schalscha et al., 1982; Stover et al., 1976; Ton et al., 1993).

High concentrations of dissolved organic matter usually are detected in the surface water of a wetland due to the degradation of plant residues. Sorption of metal ions at the water-sediment interface is then promoted by the high surface area of the organic matter. Metal ions also are removed from the aquatic system by chelation with organic ligands to form soluble or insoluble organo-metallic complexes.

Lead in the environment can be immobilized by several other factors as well, including cation exchange with clay minerals, precipitation with inorganic phosphates and carbonates, and chelation with humic substances (Saar and Weber, 1980). Perdue and Lytle (1983) pointed out that the highly diverse, acidic functional groups of humic substances are directly involved in metal complexation reactions.

Humic compounds with reactive functional groups such as hydroxyl, phenoxyl, and carboxyl also form coordination complexes with metallic ions. Carboxyl groups in

particular play a predominant role in metal binding by both humic and fulvic acids (Alloway, 1990).

In a study of humic substances, Stevenson (1982) pointed out that, unlike simple biochemical compounds and low-molecular-weight fulvic acids, humic acids tend to form complexes with metal ions that are insoluble and thus relatively unavailable to plants. This finding is in agreement with Leeper's study (1978), which suggested that Pb in highly organic soil is so tightly complexed that it cannot be taken up by crop plants. Davies (1990), in a review of the behavior of Pb in soil, also pointed out that high-molecular-weight humic acids contribute most to the immobilization of Pb, and that Pb is bound through coordinate binding by free electron pairs.

An important property of humic substances is their ability to interact with metal ions. The nature of the bond between humic substances and metallic ions ranges from electrostatic, such as metal adsorption or ion-exchange reactions, to covalent, as in the formation of organic complexes and chelates. At environmental pH values, Pb, Cu, and Fe form hydroxo-complexes with humic substances, and it is believed that these complexes are largely insoluble (Francois, 1990; Rickard and Nriagu, 1978)

When attempting to quantify the extent and stability of complexation between heavy metals and humic substances, available metal binding-capacity of the organic matter along with the associated conditional stability constants are the most commonly employed parameters (Tuschall, 1981). Such values provide a quantitative measure of the affinity of the metals for the ligands, and are of importance in determining the fate of metals in the environment (Rickard and Nriagu, 1978; Saar and Weber, 1980; Sposito et al., 1981; Stevenson, 1976, 1982).

Available metal-binding ability, also called complexing capacity, is defined as the quantity of metal-ion titrant that can be complexed by the ligands in an environmental water sample (Truitt and Weber, 1981a, 1981b; Tuschall, 1981). Such stability constants are

classified according to the form of reaction as complexation constants (Stevenson, 1982). The basic metal-organic complexing reaction is

$$jM + iA \iff M_jA_i$$

where M is the metal ion and A is the ligand in equation.

The stability constant, K, is defined as

$$K = \frac{(M_jA_i)}{(M)^j(A)^i}$$

Two general approaches have been utilized in the investigation of metal complexes with humic substances. First, metal ions are regarded as the central group of the complex, with the *ligands* as the central group constituting the second case. When the metal ion functions as the central group (the most common case), the formation of MA_i complexes is considered. In this case, the overall stability constant for each added ligand usually is referred to as the conditional stability constant, β (Stevenson, 1982).

The stepwise reactions can be illustrated as follows:

$$A^- + M^{2+} \underset{\Longleftrightarrow}{\overset{k_1}{}} MA^+ \; ; \qquad A^- + MA^+ \underset{\Longleftrightarrow}{\overset{k_2}{}} MA_2$$

The overall reaction is described as

$$2A^- + M^{2+} \underset{\Longleftrightarrow}{\overset{\beta}{}} MA_2$$
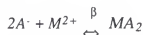
with the conditional stability constant β therefore being given by

$$\beta = \frac{MA_2}{(A^-)^2(M^{2+})}$$

Humic substances have been reported to complex both divalent and trivalent metal ions (Stevenson, 1982), with the metal most strongly bound by humic substances reportedly being Cu^{2+} (Rickard and Nriagu, 1978; Stevenson, 1982; Thurman, 1985). The respective stability constants decrease in the order $Cu^{2+} > Fe^{2+} > Ni^{2+} > Pb^{2+} > Co^{2+} > Zn^{2+}$ (Rickard and Nriagu, 1978; Stevenson, 1982). However, due to different experimental conditions and methods for the determination of stability constants, another sequence of constants was suggested by Friedland (1990) as follows: $Pb^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+}$.

In prior studies of Pb-fulvic acid (FA) interactions, the logs of the stability constants (β) have been reported to range from 2.7 to 3.09 at pH 3.5. Increased ionization of the functional groups (especially COOH) at higher pH (5.0) was attributed to increased stabilities, ranging from 4.0 to 6.13 (Rickard and Nriagu, 1978; Stevenson, 1982). From early studies of the complexation of Pb by humic substances, some other available stabilities for the complexes are included in Table 2-8. Little information is available for Pb-humic acid complexes, aside from that shown for pH 7.

2.5 Heavy Metal Movement, Distribution, and Availability

The bioavailability and recycling of heavy metals are highly dependent on the chemical phase with which a metal is associated in sediments. Thus, the quantitative distribution of metals among the various phases is of considerable importance, as well as the environmental changes which influence such distributions. A variety of factors such as the content of soluble organic matter, pH of the water, and the dissolved-sulfide concentration would be expected to affect the rate and degree of metal immobilization by peat sediments (Saar and Weber, 1980; Salomons and Förstner, 1984; Ton, 1990).

The behavior of trace metals in aquatic systems is highly complex due to the number of possible interactions and changes in various external factors including pH, redox potential, and concentrations of interactive substances. Metal ions can exist in free ionic form and also as complexes with inorganic species such as hydroxides, carbonates, and sulfates, along with a wide variety of organic ligands (Harper, 1985; Nriagu, 1978a). The solubility of each such species is regulated primarily by pH.

The pH and redox potential·are two major factors determining the chemistry of heavy metals in sediments. Harper (1985) conducted a series of experiments to characterize the effects of redox potential and pH on heavy metals. Three major patterns for the release of heavy metals were suggested:

1. some metals are released at a greater rate at high redox potential;

Table 2-8. Log of the conditional stability constants (β) of Pb-humic substances complexes.

Type of complex*	pH			Reference	**
	3	5	7		
Pb-AHA(S)	-	-	6.50	Guy and Chakrabarti, 1976	1
Pb-AHA(W)	-	-	5.30	Guy and Chakrabarti, 1976	1
Pb-SFA	2.60	4.10	-	Buffle et al., 1977	1
Pb-SFA	-	-	3.64	Ramamoorthy and Kushner, 1975	1
Pb-SFA	3.21	-	-	Ramamoorthy and Manning, 1974	1
Pb-SFA	2.60	4.10	-	Schnitzer and Hansen, 1970	1
Pb-SFA	3.10	6.10	-	Schnitzer and Skinner, 1967	1
Pb-SFA	-	4.22	-	Sposito et al., 1981	2
Pb-SFA	2.70	4.00	-	Stevenson, 1982	3
Pb-WHA	-	-	6.00	Buffle et al., 1977	1
Pb-WHA	-	-	5.50	Buffle et al., 1977	1
Pb-WFA	-	-	5.10	Buffle and Greter, 1979	1
Pb-river water	-	-	3.95	Ramamoorthy and Kushner, 1975	1

* Abbreviations: AHA, Aldrich humic acid; SFA, soil-derived fulvic acid; WHA, water-derived humic acid; WFA, water-derived fulvic acid.
** Reference cited from: 1- Sarr and Weber, 1980; 2- Sposito et al., 1981; 3- Stevenson, 1982.
(S): Strong sites; (W): Weak sites.

2. some metals are released at a greater rate at low redox potential; and

3. some metals seem to be released at rates independent of redox potential.

Lead has been characterized as demonstrating the first pattern. At a selected pH (5.0), the release of Pb from sediments increases with increasing redox potential. The maximum release rates for Pb were also found at low pH, ranged from 5.0 to 8.5, with any redox potential.

In the previous discussion of Pb transport and transformations during the hydrocycle (section 2.4.2), the speciation of Pb proved to be the key to understanding the fate of Pb in wetland ecosystems. Bioavailability as well as the interactions between Pb and abiotic reservoirs is mostly determined by speciation of the metal (Rickard and Nriagu, 1978).

Many equilibrium models based on thermodynamic data have been used to predict the chemical mobility of inorganic metal species in freshwater under various environmental conditions (Förstner and Witman, 1979; Stumm and Morgan, 1981). Surprisingly, little has been mentioned concerning organic-metal species, even though organic matter is continually being added or deposited in most natural systems.

The most commonly used model is the pH-redox potential diagram, i.e., an Eh-pH diagram. The importance of an Eh-pH diagram is that it provides an aid in the interpretation of equilibrium constants, by permitting the simultaneous representation of many reactions (Brookins, 1988; Harper, 1985, Pourbaix, 1966).

There are two important boundaries within the stability region for water in a generic Eh-pH diagram, where P_{O_2} and P_{H_2} are set at 1 bar, respectively (Figure 2-3). The first is located between reduced and oxidized sulfur species. This sulfide-sulfate boundary separates overall chemically-reducing conditions from mildly-oxidizing conditions. The second boundary, for organic carbon oxidizing to carbonate, is also shown on Figure 2-3. Oxidizing, transitional, and reducing environments are indicated by 1. mine water; 2. rain; 3. streams; 4. normal ocean water; 5. aerated saline water residues; 6. ground waters;
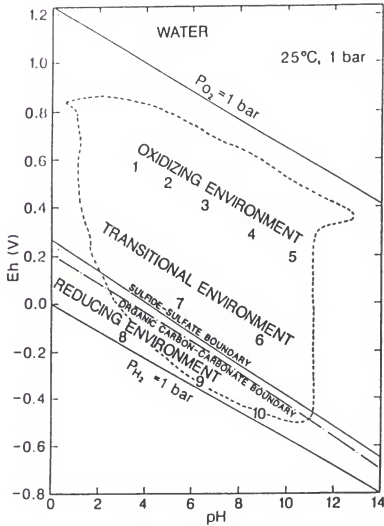
Figure 2-3. Generic Eh-pH diagram for water systems, showing different redox environments. (After Brookins, 1988)

7. bog waters; 8. water-logged soils; 9. black marine waters; and 10. organic-rich saline waters (Brookins, 1988).

Any metals released by destruction of organic material may oxidize subsequently to form carbonates or sulfate minerals at thermodynamic equilibrium (otherwise, amorphous precipitations). Some of the relevant wetland-type environments are indicated on Figure 2-3. These environments include

> (7) Bog waters, which tend to be mildly reducing and acidic. Such waters cross the sulfide-sulfate boundary, as shown in the diagram.

> (8) Water-logged soils, also found under reducing and acidic conditions.

In wetland systems, the release of organic acids from degraded humic substances decreases the pH of the surface water, which can range from 3.5 to 5.0 (Mitsch and Gosselink, 1986). With a lower pH and a higher organic content, Pb-organic interactions may dominate the speciation. However, under reduced environments, the solubility of many metal species is regulated by the SO_4-S - H_2S system (Förstner and Witman, 1979).

Another Eh-pH diagram for part of the system Pb-S-C-O-H is given in Figure 2-4. The assumed activities of dissolved species are list as follows: Pb = 10^{-6} M, S = 10^{-8} M, C = 10^{-3} M. Generally, the SO_4^{2-} species is dominant under oxidized conditions. Under reduced and acidic conditions, however, SO_4^{2-} is reduced to H_2S but Pb^{+2} remains unchanged. This results in a very small field of Pb^{+2} at pH below 0.4 (Brookins, 1988). The species (H_2S), in turn, is in equilibrium with HS^- and S^{-2} according to the following reactions:

$$H_2S = HS^- + H^+ = S^{-2} + H^+$$

Since most of the sulfide (S^{-2}) forms of heavy metals are highly insoluble, an increasing sulfide concentration generally results in increasing insoluble forms of metal species, such as Pb-sulfide.

Florence and Batley (1980) pointed out that, as the pH of surface water is lowered, the fraction of ionic Pb is increased. The extent of trace-metal adsorption onto solid
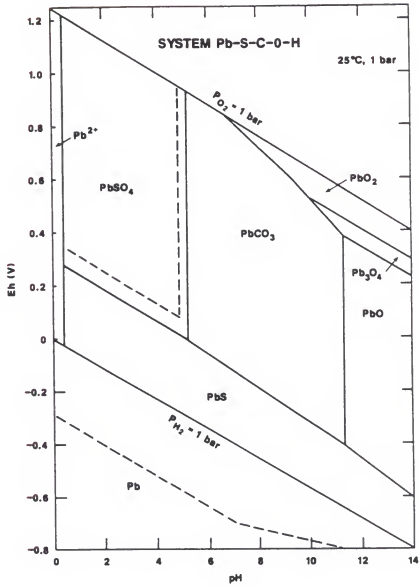
Figure 2-4. Eh-pH diagram for some of the Pb species in the system Pb-S-C-O-H:
Pb = 10^{-6}, S = 10^{-3}, C = 10^{-3} M, and Temperature = 25 °C. (After
Brookins, 1988)

particles in freshwater is thus highly pH dependent. In water of low pH, i.e., 3.5 to 5.0, little Pb is expected to be adsorbed onto inorganic colloids. Direct adsorption of Pb onto most inorganic adsorbents generally occurs at pH values 6.0 and above.

However, Pb usually complexes with organic ligands, followed by the adsorption of these complexes onto hydrous oxide solids or other organic particulates (Huang et al., 1977). The maximum adsorption of complexing ligands onto oxide surface sites was observed at a pH approximately equal to the pKa of the associated ligands (Davis and Leckie, 1978). In organic-rich freshwater, the pH generally ranges from 3.5 to 5.0, which is close to the pKa of natural humic acid, i.e., 2.5 to 4.5 (Tipping et al., 1988). Therefore, the high levels of organically bound lead in several early reports suggest that organic Pb complexes might be an important metal species in sediments (Garlaschi et al., 1985; Rudd et al., 1988; Schalscha et al., 1982; Stover et al., 1976; Ton, 1990; Ton et al., 1993).

2.6 Rehabilitating Damaged Ecosystems

An ecosystem is a living community and a nonliving environment which function together as an ecological system (Odum, 1959). If the system is altered due to human activities or natural processes, the ecological structure of the community and the ecological functions of the system are either eliminated or substantially changed. In some cases, some of the existing species may be replaced relatively quickly, while in others the system may not be restored within a decade or even a century (Cairns, 1988).

The degraded habitats resulting from heavy-metals contamination tend to be unique. They represent major changes in the environment, analogous to the creation of new islands. McNeilly (1987) reported that the number of species growing on heavy metals-contaminated sites tend to be limited. From a survey of the flora at abandoned Pb and Zn mines in southeastern Wisconsin, it was noted that the number of flora species decreased and the degree of percentage cover increased with increasing age of the site (Wickland, 1990).

To obtain a normal ecosystem after metals contamination, effects of the metals have to be dealt with completely (Bradshaw, 1987). A covering of organic matter to bind any available metals was originally thought to be effective, but the release of toxic metals after the subsequent degradation of organic matter also needs to be considered.

Facilitation of coverage of a metal-contaminated site by perennials is possible only if metals toxicity can be decreased, either by the formation of less toxic and/or less plant-available metal-complexes or by dilution of the metals concentrations (Ernst, 1990).

A degraded ecosystem obviously provides an extreme environment for plant growth. In some cases, degradation may be so extreme as to completely devastate the original ecosystem (McNeilly, 1987). Although a particular species may have the potential to evolve metal tolerance, evolutionary change of genetic characteristics via natural processes is considered to be an extremely slow process (Bradshaw, 1987). An artificial selection of suitable species, therefore, is a practical approach for ecological restoration.

2.7 System Analysis

The complexity of interactions between human activities and the natural environment has increased due to the rapid development of urban areas and associated economic systems. Many studies have been conducted to aid in incorporating environmental values into planning and decision-making processes (Keller, 1992; Odum, 1983, 1988a; Odum et al., 1988; Pritchard, 1992). The major effort of most such evaluations has been focused on measuring the impacts of development and the benefits from preserving the degraded environment.

Environmental systems analysis seeks to develop a package of basic principles that govern the interactions between natural and human systems. The principles are then used to analyze the structures of the systems and to predict their performance under different conditions (Odum, 1983, 1988a).

When simplified components of a system interact according to some kind of process, a systems diagram can be drawn. Energy symbol language, analogous to that used in a simple circuit diagram, facilitates the associated network of thinking and computer simulation. The diagrams also can help nontechnical people to understand how environmental systems work (Odum, 1983, 1988a).

2.7.1 Emergy Analysis Theory

Starting in 1983 the concept of embodied energy was renamed "EMERGY" and given the unit, emjoule (Odum, 1983). Emergy is the energy of one form directly and indirectly required to do environmental work (Odum, 1986; Scienceman, 1987). Therefore, emergy is used as the principal conceptual tool for expressing the interrelationship of energetic flows and resource quality, and for linking together systems of the natural environment and human economy (Odum, 1971; 1988a).

As a result, emergy analysis is a type of embodied energy analysis that can provide common units (emergy) for comparison of environmental and economic goods, which cab be done by summing the energy of one type required directly or indirectly for the production of goods (Odum, 1988a). Different energy forms contribute in turn to the ecological processes and to economic activities. The actual energy of various kinds which is used for production processes is said to be "embodied" in the product. For example, the production of a piece of paper from wood may require direct energy from sunlight, wind, rain, chemicals, equipment, and human labor. Wind and rain energy require solar energy for their production. Chemicals, equipment and human labor are transformations of fossil fuel energy, which also required solar and geological energy. The amounts of solar energy necessary for each input, then, can be back-calculated.

In emergy analysis, the quality of each form of energy is taken into account by multiplying each quantity of energy by its solar transformity. Solar transformity is defined as solar emergy per unit energy, sej/j (Odum, 1988a, 1988b). Energy of high transformity

has more emergy and is high in its quality of effect. For clarification, Table 2-9 provides a summary of definitions embodied in the concept and in the emergy-evaluation terms.

2.7.2. Emergy Evaluation

"Price" is the amount of money needed to buy a certain unit of goods or services. It reflects the relationship between the flow of goods and the flow of money. Commonly it is referred to as market value, defined in terms of what people are willing to pay (Baumol and Blinder, 1985). Natural inputs and human services are each considered to contribute to economic growth. However, it is difficult to place a market value on natural services. This is because money is paid only for human services, with nature never getting paid (Odum et al., 1988).

To evaluate the contribution of natural services, solar emergy has been adopted as a common measure. All energy sources that contribute to the economy are calculated in terms of solar emergy. By dividing the total solar emergy of the economy by the gross national product (GNP), the emergy-money ratio is obtained (Odum et al., 1988). In other words,

$$\text{Emergy-money ratio (sej/\$)} = \frac{\text{Total solar emergy of the economy (sej)}}{\text{Gross national product (GNP) (\$)}}$$

By dividing the solar emergy of any environmental inputs by the emergy-money ratio, the amount of natural contributions, in terms of macroeconomic value, can be estimated as

$$\text{Macroeconomic value (\$)} = \frac{\text{Emergy (sej)}}{\text{Emergy-money ratio (sej/\$)}}$$

Decisions on the use of resources in ecological management cannot be made correctly using money because money is only paid for services, but an emergy comparison can be prepared for choosing among environmental alternatives. The net emergy yield of an energy resource and/or an ecological process is the emergy yield after subtracting the emergy for processing. Primary sources and/or ecological processes can be evaluated with the net emergy yield ratio, which is the ratio of the emergy yield divided by the emergy used for processing. In other words,

Table 2-9. Definitions of emergy evaluation concepts.

* Emergy	Energy of a single type required directly and indirectly for transformations in order to generate a product or service.
Solar emergy	Solar energy required directly and indirectly to produce a product or service (units of solar emjoules - sej).
Transformity	Emergy per unit energy required for a given product or service in a system.
Solar transformity	Solar emergy per unit energy (units of solar emjoules/joule - sej/J).
Emergy per unit mass	Emergy of a single type required to generate a flow or storage of a unit mass of a material (units of sej/g).
Empower	Emergy flow per unit time, usually per year (units of sej/yr).
Emergy/Money ratio	Ratio of emergy flow to money flow, commonly for a state or nation, calculated as annual emergy use divided by the value of the gross national product (units of sej/$).
Net emergy yield ratio	Ratio of the emergy yield divided by the the emergy used for processing, served as an indication of contribution to the economy.
Emergy investment ratio	Ratio of emergy brought into an area from the economy and from environmental resources, served as a measure of economic loading of the environment.

* Sources: Odum, 1988a, 1988b, 1991, 1993; Odum et al., 1988.

$$\text{Net emergy yield ratio} = \frac{\text{Yield emergy}}{\text{Feedback emergy}}$$

Typical net emergy yield ratios of fuels and environmental products range from 1.06 to 12.0 (Odum, 1993). Higher net emergy yields of energy resources and ecological processes indicate greater contributions to the economy, and therefore, are more economically competitive than lower ones.

The ratio of emergy brought into an area from the economy and from environmental resources which are used to describe the interaction, is the emergy investment ratio (Odum, 1993). It can be obtained as

$$\text{Emergy investment ratio} = \frac{\text{Purchased emergy}}{\text{Environmental emergy}}$$

This index is a measure of economic loading of the environment and also can be used to determining the competitive value of an ecological process. Lower emergy investment ratio of a proposed project usually means that it requires lower purchase costs from the economy and more support from the environment. Environmental processes with higher emergy investment ratios usually require less environment to support each unit of economic activity. Thus, the impacts on them are heavier and more of their emergy is used up without being reinforced.

3.1 Study Area

3.1.1 Site Description

The area selected for this investigation was a cypress/black gum wetland named Steel City Bay in Jackson County, Florida. This area received large quantities of Pb carried in acid waters draining from Sapp Battery Service, Inc. (now an EPA Superfund site) from 1970 to 1980. The Sapp Battery site is located 3.2 km south of the I-10 interstate on US-231 near the intersection of US-231 and county road 276 (Figure 3-1).

This study site has a moderate climate, with temperatures ranging from 21°C to 32.5°C in summer and 6°C to 18.5°C in winter. Annual rainfall averages 148 cm. The rainy season, which generally begins in early December and ends in late April, and summer thunderstorms contribute most (up to 90%) of the precipitation (U.S. Soil Conservation Service, 1979).

The Sapp Battery site is located on a topographically high area relative to the elevation of surrounding swamps and streams, with the general area of the study site receiving rainfall as its only major water source. Surface water, including acid discharge from the Sapp Battery site, drains to the south and east into the West and East Swamps, and then flows into Steel City Bay. This series of cypress swamps empties into Little Dry Creek approximately 1.6 km away. Eventually, this drainage system discharges to the Chipola River and the Gulf of Mexico (Figure 3-2).
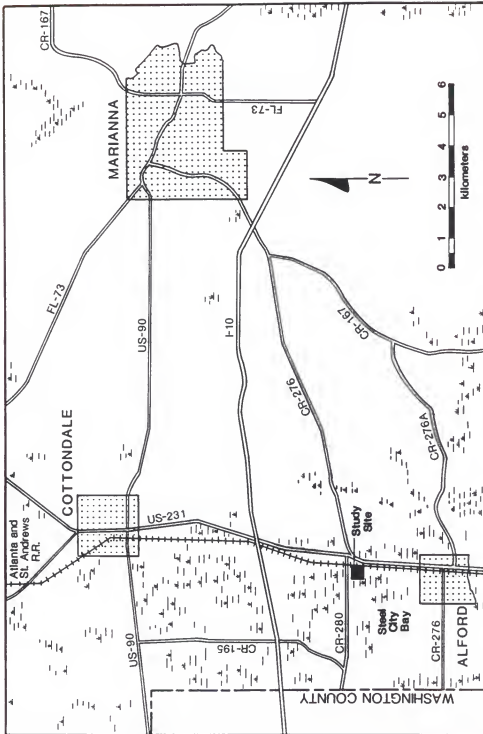
Figure 3-1. Study site location near the Steel City Bay, Jackson County, Florida.
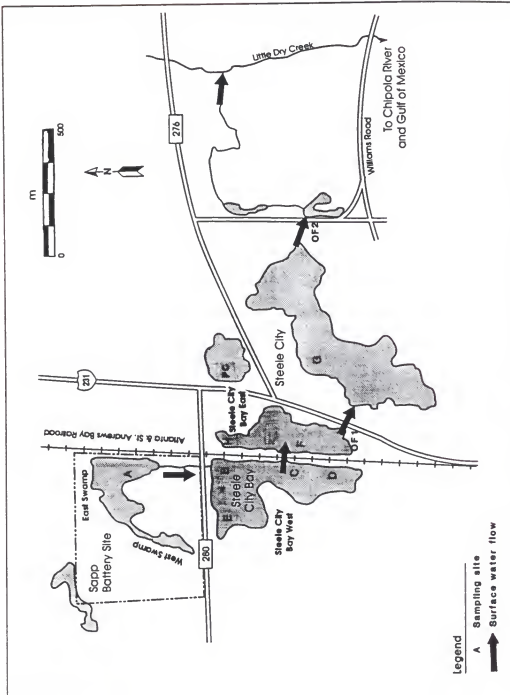
Figure 3-2. Location of sampling sites, and surface water drainage pattern, within the study area.

The off-site wetland areas occupy approx. 24.9 ha. and are separated into three major parts by the Atlanta and St. Andrews Bay railroad tracks and US-231 (Figure 3-2). Hydrology of Steel City Bay West has been affected not only by the railroad berm and culvert, but more recently by a beaver dam in the upstream side of the culvert connecting the East and West wetlands under the railroad. As a result, this wetland is continually flooded except during extreme drought periods. In contrast, water levels of the Steel City Bay East wetland vary seasonally.

The forest species covering most of the Steel City Bay wetlands are primarily cypress (*Taxodium* sp.) and swamp tupelo (*Nyssa* sp.). Other woody species are also observed. Open water areas are thickly populated with water lily (*Nymphaea odorata*) and baldderwort (*Utricularia* sp.). Submerged aquatic plants such as eel grass (*Eleocharis* sp.) are seen in the East Swamp (site A) exclusively.

3.1.2 Site History

Sapp Battery Service, Inc. initiated an operation involving the cracking open of used automobile batteries to recover Pb in 1970. Beginning as a small operation, the business gradually expanded to process as many as 50,000 used batteries per week in 1978 (Mundrink, 1989; Trnovsky et al., 1988). The standard procedure for disposing of the wastes was to dump the acid from batteries outside the plant. The acid then ran through adjacent wetlands and eventually was discharged to Steel City Bay.

While the plant was in operation, complaints about damage to cypress trees in adjoining wetlands of Steel City Bay were reported by 1977. In response to enforcement actions by the Florida Department of Environmental Regulation (FDER), the Sapp Battery management undertook several steps to alleviate the problem. After several efforts failed to correct the problem, the owner of the facility abruptly closed the plant and abandoned the site in January, 1980. Although the plant was abandoned, the residual acid and heavily

contaminated soil and sediment still have a strong influence on the adjoining wetland ecosystem, have potential for groundwater contamination, and pose a risk to the potable water supply (Watts, 1984).

3.1.3 Previous Studies

In response to citizens' concern about high acidity and Pb concentrations in Steel City Bay, the EPA undertook emergency cleanup actions under provisions of the Clean Water Act, Section 311. Despite these actions, the EPA still failed to correct the problems. In October, 1981, the Sapp Battery site was proposed for inclusion on the National Priorities List (NPL) and was included on the final NPL in August, 1982.

After that date, the EPA cooperated with the FDER in conducting the Remedial Investigation/Feasibility Study (RI/FS). In this study, the on-site soils, groundwater, surface water, and sediments were examined. Results of these sampling activities are given in detail in the final FDER report (Watts, 1984). In general, the results indicated that on-site soil, surface water, sediments, and groundwater were heavily contaminated with several heavy metals, most notably Pb.

In early 1985, Ecology & Environment, Inc., (E&E) became involved in field investigations to further delineate the extent of the contamination. Another draft feasibility study was completed by E&E in January, 1987. A summary of these investigations was reported earlier (Ton, 1990). The results indicated a dramatic decrease in Pb concentrations of surface waters from those reported by Watts (1984), though the concentrations of Pb in sediments still remained high.

3.2 Field Studies

This study expands earlier work performed to evaluate the environmental impact of metal wastes. Previously, Ton (1990) and Pritchard (1992) showed the capability of wetlands for Pb retention and the value of wetlands retention of Pb to society. To

characterize the impact and fate of leaded, acidic wastewater through a wetland ecosystem, two major types of field studies were conducted: collecting ecological data (mostly with respect to biota) and routinely monitoring Pb concentrations in the environment.

3.2.1 Sampling Procedures

Samples for metals analysis were collected from locations designated on the site map (Figure 3-2). Samples were taken from upstream near the original source of Pb and proceeding downstream in a series of sites: A, B, C, F, OF1, G, and OF2. Descriptions of the sampling sites are given in Table 3-1. Sites D and H are areas peripheral to the main flow path through the system. Site E, an area receiving battery plant wastewater discharge historically, was selected due to a high level of Pb in its sediment. An isolated, open-water cypress pond also was chosen to serve as an experimental control, site PC. Therefore, 11 sample sites were included in the study. Sediment, surface water, vegetation, and animal samples were collected during the period from April, 1989 to September, 1992.

Surface water samples were collected by submerging acid-rinsed Nalgene polyethylene bottles into the standing water. Water samples for nutrient analysis were preserved in the field with 0.2% (v/v) H_2SO_4, and samples for the metal analyses were preserved with 0.2% (v/v) HNO_3. Conductivity was measured either in the field or in the laboratory prior to acidification. Water pH, temperature, and water depth were measured at all surface-water sampling locations. Redox potential and dissolved oxygen measurements were performed once, in June of 1991. A trip blank sample bottle with deionized distilled (DDI) water was carried for quality assurance and quality control (QA/QC) purposes. All water samples were transported to the laboratory and kept refrigerated at 4°C until analysis.

Sediment samples were collected from the same locations as the surface water samples. Sediment sampling equipment included a 4-inch bucket auger which was constructed from stainless steel. Sampling was conducted at depth intervals of 0 to 0.5 feet (0-15 cm), 0.5 to 1.0 feet (15-30 cm), and 1.0 to 1.5 feet (30-45 cm) for the first two

Table 3-1. Description of the sampling sites.

Sampling Site*	Site Description
A	Located in East Swamp, shallow open water, poorly decomposed organic matter, eel grass predominant.
B	South of CR 280 in Steel City Bay West, 240 m from site A, open water covered by dead logs, poorly decomposed organic matter, water lily predominant
C	South of culvert in Steel City Bay West, 444 m from site A, open water, poorly decomposed organic matter with sandy clay, water lily predominant
D	South end of Steel City Bay West, 587 m from site A, poorly to less decomposed organic matter, deep open water, water lily predominant, recovering black gum community
E	West of Steel City Bay West, shallow open water, poorly to less decomposed organic matter, water lily and Juncus predominant
F	South of culvert in Steel City Bay East, 459 m from site A, open water with few black gum, decomposed organic matter with sandy clay, water lily predominant
G	Across US 231 > 900 m from site A, decomposed organic matter with fine sandy loam, water lily dominant, open water, black gum community dominates the surrounding areas
H	Opposite from site B in Steel City Bay East, shallow water under a canopy of black gum and few cypress, poorly decomposed organic matter, black gum predominant
OF1	Before the culvert under US 231 in Steel City Bay East, shallow open water, decomposed organic matter with fine sandy loam, surface water outflow point from Steel City Bay
OF2	End of the study area, open water channel, sandy clay, water lily predominant
PC	Near the intersection of US 231 and CR 276, open water deep near the center, decomposed organic matter, water lily predominant

* See Figure 3-2 for the location of each sampling site.

years, 1989-1990. Only the upper layer of sediment, 0-15 cm, was chosen for sampling during 1991-1992. Sediment core samples were stored in heavy-duty, zip-lock plastic bags. All samples were stored in coolers, transported to the laboratory within 6 hrs., and frozen until analysis.

Leaves, tree stems, aquatic plants, and algae in the wetland were collected as vegetation samples. Tree stems were cut with an ax, while other samples were collected directly by hand. Aquatic plants were washed with surface water to remove attached sediment. Vegetation samples were stored in heavy-duty, zip-lock plastic bags for transport back to the laboratory. Fish samples and beaver's liver were collected once, in October of 1989, as animal samples. All samples except those for vegetation species identification were frozen until analysis. A detailed description of the field sampling schedule is listed in Table 3-2.

3.2.2 Analytical Methods

3.2.2.1 Sample pretreatment

Several procedures for sample pretreatment were performed. For surface water, 200 ml of acidified sample was concentrated on a hotplate to a final volume of 10 ml. Surface waters were filtered through a 0.45 μm membrane prior to nitrite+nitrate and ammonia analyses. Digestion of surface water was necessary for the total Kjeldahl nitrogen (TKN), EPA method 351.2, and total organic phosphorus analyses, EPA method 365.4.

Sediment, vegetation, and animal samples were dried in an oven for 24 hrs at 105°C. Dried samples were ground and passed through a No. 40 sieve (Tyler equivalent size, 35 mesh). Due to small quantity, no grinding was applied to fish samples. Nitric acid and H_2O_2 were used to digest the solid samples (Delfino and Enderson, 1978). Vegetation samples for species identification were typically dehydrated prior to identification.

Table 3-2. Field sampling schedule at study area from April, 1989
to September, 1992.

Date	Samples Collected	Field Measurements
Apr-89	Surface water Sediment Vegetation	Water depth Temperature pH & electrical conductivity
Oct-89	Animal (Fish and beaver's liver)	*
Feb-90	Surface water Sediment Vegetation Benthic organisms	Water depth Temperature pH Diurnal oxygen measurement
Aug-90	Surface water Sediment Vegetation	Water depth Temperature pH & electrical conductivity
Sep-90	Surface water	pH & conductivity
Jun-91	Surface water Sediment	Water depth Temperature pH & electrical conductivity Redox potential Dissolved oxygen
Jul-91	Vegetation	Vegetation productivity
Jan-92	Surface water Sediment Vegetation	Water depth Temperature pH & electrical conductivity
May-92	Surface water Sediment Vegetation	Water depth Temperature pH & electrical conductivity Vegetation diversity
Sep-92	Vegetation	Vegetation diversity

* field measurements not made.

3.2.2.2 Instrumental analyses

The analytical methods used to determine water quality parameters in this study followed those of the U.S. Environmental Protection Agency (EPA, 1979) and/or Standard Methods (APHA et al., 1985).

To insure validity of the data, certain actions were taken to meet acceptable quality assurance and quality control (QA/QC) requirements. The QA/QC program in this study included the analysis of EPA-known evaluation samples in every analysis series, the running of 10% duplicate samples, and checking the recoveries of standard-solution spikes.

All of the metal analyses were performed using flame atomic absorption spectrophotometry (AAS). A Perkin-Elmer model 5000 AAS with double-beam system and air-acetylene fuel was employed with an instrumental detection limit for Pb equal to 0.01 mg/L or 10.0 μg/g for solid samples.

Dissolved oxygen (DO) was measured using a YSI model 54A oxygen meter with an instrumental detection limit of 0.1 mg O_2/L. Winkler titrations were performed to confirm the DO meter readings both before and after each sampling trip.

Redox potential and pH measurements were carried out using a Fisher model 900 pH meter. Instrumental calibration for the pH meter was achieved by using two standard buffer solutions at pH 4.0 and 7.0. The manufacturer's calibration procedures for redox potential measurements were followed as well.

Electrical conductivity was measured using a Fisher digital conductivity meter with an output range of 0 to 200 S/cm. Water depth was measured using a meter stick, with every datum representing an average of three measurements within a square meter area. A standard thermometer with a range from -10°C to 110°C was used to obtain the temperature readings.

3.2.2.3 Bioconcentration factor determinations

The accumulation of chemicals and metals over time in an organism is observed in many species and is termed its "bioconcentration factor" (BCF) or "enrichment ratio" (Kelly, 1988; O'Connor et al., 1988; Stumm and Morgan, 1981; Thomann, 1988). Bioconcentration is a general biological process. Results of the BCF measurements indicate that organisms accumulate chemicals directly from ambient environments, i.e., water and sediment.

Values of the BCFs were obtained by dividing the equilibrium concentrations in the organisms by the concentrations in the environment. Thus, the BCF of vegetation is given by

$$BCF = \frac{\text{concentration in plant}}{\text{concentration in sediment/water}}$$

The BCF for different vegetation samples was determined. Relationships of the BCF to pH and to aqueous concentrations also were discussed.

3.3 Microcosm Study

Microcosms have been recommended for assessing ecological effects of toxic chemicals (Pritchard and Bourquin, 1984). Some of the successful experiments mentioned earlier (Section 2.2) also encouraged the use of microcosms to examine the impacts of acid and Pb to wetland communities. Small size, replicability, and easy access to the laboratory are among the advantages of using microcosms instead of a field approach to the investigation.

3.3.1 Experimental Design

Pond cypress (*Taxodium ascendens*) and black gum (*Nyssa sylvatica*) were selected for the study to simulate the original wetland communities. Sixty seedlings of each species were used for testing. Three different pH values, 2.0, 4.0, and 7.0, and Pb

concentrations, 0.0, 0.5, 5.0 mg/L, were employed. Decreasing concentrations of Pb in the treatments provided a comparison of the impacts of Pb. Solutions with different pH were used to check the associated acid effects. A total of nine treatment combinations were employed.

The experimental design matrix for the microcosms is shown in Table 3-3. Six replicates of cypress and black gum were used for each treatment. Six additional seedlings served as the experimental control for each species. Nine units without seedlings were used as blanks for each treatment. In total, 129 test units were used for the microcosm study.

Experimental microcosms were set up in a greenhouse near the Center for Wetlands, University of Florida, in June, 1991. The microcosms were confined to two regions, each with an area of 1.8 m x 1.8 m. Each region was divided into 8 rows and 8 columns, with the columns designated by letters from A to H. The rows were designated by numbers from 1 to 16. The combination of a number and a letter thus indicated each individual test unit. Totally, there were 128 sections created for the test. To compensate for the difference among test units (129) and created sections (128), a section, termed 16I, was added to the last row.

To satisfy statistical requirements, the seedlings were set in random order. They were planted individually in plastic double pots, using a mixture of potting soil, peat, pine bark, sand, clay, etc., from a commercial supplier (Traxler Peat Co., Orange Heights, Florida) as the bedding substrata. One teaspoon of fertilizer (Osmocote 17-6-10) was spread under the root zone of each plant before replanting to provide the nutrients required for growth. In this study, reagent-grade sulfuric acid and a standard solution of Pb from Fisher Scientific, Inc. were used to adjust the pH and provide the source of Pb, respectively.

A distribution system with automatic irrigation programming was constructed to perform the chemical treatments. The structure of the distribution system is shown in

Table 3-3. Matrix of the experimental design for the microcosm study

Chemical Treatments for the Microcosms			
pH[Pb]	0(W)	0.5(A)	5.0(B)
7.0(W)	1*	2	3
2.0(C)	4	6	8
4.0(D)	5	7	9

* Numbers indicate the treatment combinations.

Notes:
1. Three different pH values 7.0(W), 4.0(D), 2.0(C); and
   three Pb concentrations 0(W), 0.5(A), 5.0(B) mg/L
   were used for the chemical treatment test.

2. Six replicate seedlings of each species (cypress, black gum)
   were tested in each treatment combination.

3. Six extra seedlings served as an experimental control for
   each species, using the same conditions as treatment 1.

Figure 3-3. Each replicate sample was treated as an individual to avoid interference from all others. To standardize treatments, the test solution was delivered through polyvinyl chloride (PVC) pipe and small vinyl tube to each pot.

3.3.2 Sampling and Measurements

Initial Pb concentrations in the water, sediment, and vegetative tissue were sampled. Nominal Pb concentrations and pH of the microcosms were monitored during each time of preparation. Actual values of these chemical reagents were regularly measured in the plant pots.

The heights of the seedlings were measured with a Stanley Powerlock® II tape approximately once each month from August, 1991 through December, 1992. Growth rates of the seedlings was calculated using the net growth value for each month.

3.3.3 Statistical Analysis

A statistical analysis for multifactorial experiments was used to analyze the growth rate (Montgomery, 1984). The analysis used was a 3^2 factorial design; that is, a factorial arrangement with two factors at each of three levels. The treatment combinations for this design were shown earlier in Table 3-3.

Since there were $3^2 = 9$ treatment combinations, there were eight degrees of freedom among the treatment combinations. The main effects of pH (as X) and [Pb] (as Y) each have two degrees of freedom, and the XY interaction has four degrees of freedom. If there are n replicates, i.e., 8 in this analysis, there are $n \, 3^2 - 1$ total degrees of freedom and $3^2 \, (n - 1)$ degrees of freedom for error.

A statistical software package, MINITAB® (Minitab, Inc., 1991), available for Apple Macintosh® computers, was used for the statistical analyses. The ANOVA (analysis of variance) tables were generated, and the arithmetic means of the growth rates also were calculated. Regression analyses were also performed for the experimental control and each
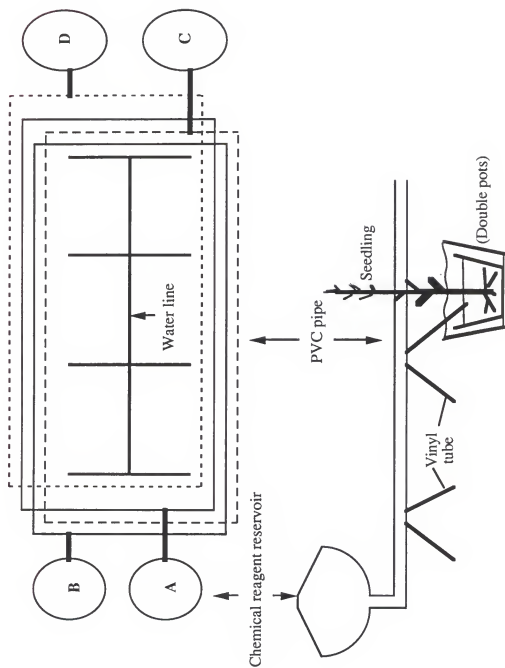
Figure 3-3. Structure of the distribution system for the microcosms.
A- 0.5mg/L Pb, B- 5.0 mg/L Pb, C- pH=2.0, D- pH=4.0

treatment combination to build a quantitative model correlating growth rates with response of the chemical treatments.

3.4 Laboratory Study

3.4.1 Fractionation of Aqueous Humic Substances

3.4.1.1 Sample collection

Aqueous samples were obtained from the control pond in the study area during field trips in June and July, 1991. A total of forty gallons of surface water were collected by submerging acid-rinsed, 10-gallon polyethylene carboys into the standing water. All water samples were transported to the laboratory at ambient temperature and processed using the methods described in the following section.

3.4.1.2 Materials and methods

Total organic carbon (TOC) in the surface water samples was measured using an Ionics model 555 organic carbon analyzer. Dissolved CO_2 in the water samples used for TOC analysis was removed by acidifying the sample with concentrated phosphoric acid and stripping with a nitrogen purge. Potassium acid phthalate solutions were prepared as standards and used to calibrate this instrument in the range 1.0 to 10.0 mg TOC/L.

Aquatic humic substances were isolated from water samples using the procedure described in Standard Method 5510 C (Clesceri et al., 1989). The basic procedure includes acidification of the 0.45 μm filtered water sample to pH 2, concentration on a macroporous resin (XAD-8), elution of aquatic humic substances by backwashing the column with dilute base (NaOH), and substitution of cations on a H-saturated cation exchange column. This procedure is similar to that used for isolation of the hydrophobic acid fraction of dissolved organic carbon from natural waters, as reported by Leenheer (1981).

The aforementioned method is an analytical isolation method. It was modified for preparative-scale isolation simply by scaling up the size of the resin column (Leenheer,

1981). It has been used to reproducibly isolate aquatic humic substances from a variety of water sources on a preparative scale (Davis, 1993). The modified schematic extraction procedure for aquatic humic substances is shown in Figure 3-4. Details of the materials and methods used for the isolation and characterization of humic substances were described by Davis (1993).

3.4.2 Complexing Capacity and Conditional Stability Constants

The stability of Pb complexes with organic substances is of major concern for the bioavailability and remobilization of Pb in sediments (Ton, 1990). Alkaline-extractable humic acid (HA) and fulvic acid (FA) are the humic substances (HS) that are most likely to affect the bioavailability and remobilization of Pb (Nriagu, 1978a; Stevenson, 1982, 1985).

Methods for quantifying metal-organic matter interactions have been reported elsewhere (Alberts and Giesy, 1983; Saar and Weber, 1980; Stevenson, 1982; Truitt and Weber, 1981a, 1981b; Tuschall, 1981; Weber, 1983). Equilibrium dialysis has been used to determine the binding capacity and conditional stability constants (Saar and Weber, 1980). A continuous-flow system was selected to perform the equilibrium dialysis, as is popular in pharmaceutical processes (New, 1990). This method has been modified for the first time to fulfill the purposes of this study, as described below.

3.4.2.1 Analytical methods

A Spectrum Molecular/Por® Polysulfone, hollow fiber cartridge (HFC) was used to perform the dialysis analysis. The HFC is a sturdy bundle composed of 90 hollow fibers with inside diameters ranging from 0.5 to 0.7 mm and a molecular-weight cutoff at 2000 Daltons. The specifications of the HFC feature a wide range of chemical compatibility and pH values, from 1 to 13.

The bundle was securely placed into a cap assembly and housed in a 1000 mL polymethylpentene (PMP) Fleaker®. A small 500 mL PMP Fleaker® was connected by Tygon® tubing to a Cole-Parmer Masterflex® pump to circulate the process solution

Isolation of Dissolved Organic Matter (Humic Substances)

Surface Water Sample

1
Filtered through 0.45μm
nylon filter, adjust pH
to 2.0 with conc. HCl

XAD-8
resin column

Nonhumic substances

2
Backwashing of the
column with 0.1 M NaOH

4
Elute through a
cation exchange column

3
Rinse with 2.0M HCl

Spectra/Gel 50X8
cation exchange resin column

Waste was discarded

Sample was collected
5
Lyophilization
Freeze-Drying at -40°C
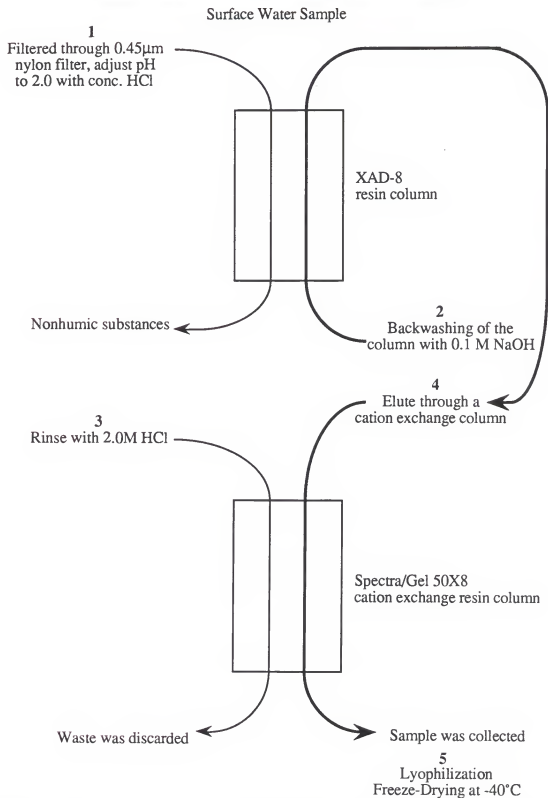
Figure 3-4. Modified schematic extraction procedure used for aquatic humic substances.

through fibers. The solution in the 1000 mL PMP Fleaker® also was circulated by pump. Two on-line sample outlets were installed to collect samples during analysis, and two Fisher stirring plates were used to blend the samples. A diagram of the apparatus used for dialysis analysis is shown in Figure 3-5.

Two humic substances, Aldrich humic acid (AHA) and aquatic humic substances (SAPP 1), were used to determine the Pb binding capacity of humic substances and the conditional stability constants of Pb-organo complexes. Solutions of humic substances, AHA and SAPP 1 (approximately 20 mg humic substances /L), were prepared in 0.1 M KNO_3 (Saar and Weber, 1980). Nitrogen gas was used to purge dissolved oxygen from the solutions before pH adjustment. The pH of the solution was adjusted as needed using dilute HNO_3 and KOH solutions (in 0.1 M KNO_3).

One liter of organic matter was used for dialysis against 0.1 L of 0.1 M KNO_3 for 72 hours. Initially, 0.5 mL of 1000 mg/L Pb standard solution was added to the electrolyte to perform the dialysis analysis, and 1.0 mL 1000 mg/L Pb^{2+} standard solution was added for overnight dialysis analysis. Solutions were equilibrated for 6 hours and 12 hours in daytime and overnight analyses, respectively, to assure sufficient equilibration (Figure 3-6). Before the next metal addition, equilibrated solutions were subsampled (ca. 2 mL) through on-line sample outlets from both Fleakers. The Pb concentrations, M_f for free metal concentration, and M_t for total metal concentration in the equilibrated solutions, were measured using flame AAS.

3.4.2.2 Complexing capacity determination and Scatchard plot methodology

When natural organic matter was dialyzed against a metal-ion solution, metal ions permeated through the membrane of the fibers and formed complexed compounds in the Fleaker containing organic matter (Alberts and Giesy, 1983; Saar and Weber, 1980; Stevenson, 1982; Truitt and Weber, 1981a, 1981b; Tuschall, 1981; Weber, 1983). At equilibrium, the free-metal concentration M_f was measured in the Fleaker containing electrolyte. Total metal concentration M_t, free plus complexed, was measured in the
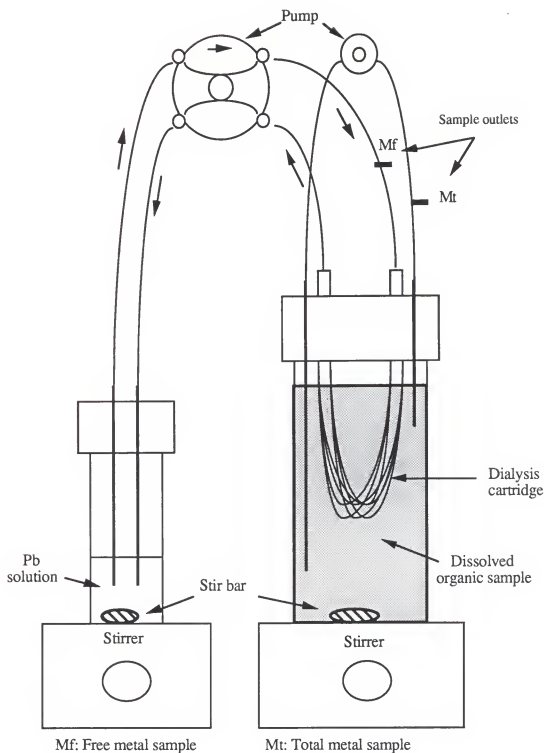
Figure 3-5. Dialysis analysis apparatus.
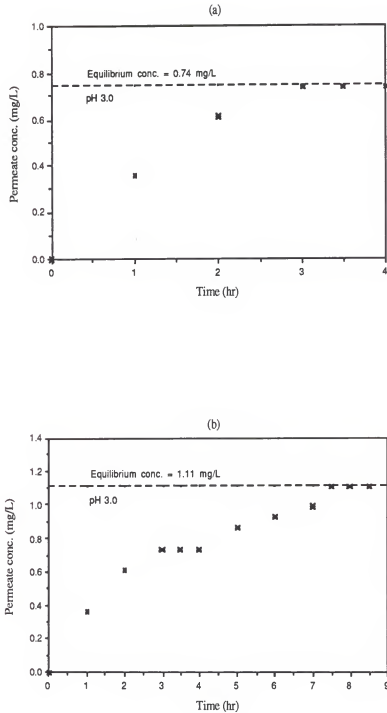
Figure 3-6. Equilibrium time following the addition of different metal solutions.

Fleaker containing organic matter. The complexed metal M_c then was calculated by a simple mass-balance equation:

$$M_c = M_t - M_f$$

The Pb complexing capacity was obtained from a plot of freely-dissolved Pb concentration vs. total Pb concentration. The curve was extrapolated to the abscissa in order to obtain the Pb complexing capacity (Davis, 1993; Truitt and Weber, 1981a).

The conditional stability constant (β) can be estimated using the Scatchard method (Stevenson, 1982; Tuschall, 1981). It was assumed that

$$\beta = \frac{M_c}{(M_f)(nA_T - M_c)} \qquad (1)$$

where A_T is the total ligand concentration, in terms of humic substances, and n is the number of binding sites per ligand molecule.

Equation (1) can be rearranged to

$$\frac{M_c}{(M_f)(A_T)} = \beta [n - \frac{M_c}{A_T}] \qquad (2)$$

By substituting V for $\frac{M_c}{A_T}$, the final form of the equation becomes

$$\frac{V}{M_f} = \beta (n - V) \qquad (3)$$

Thus, a plot of $\frac{V}{M_f}$ vs. V should produce a curve with slope $-\beta$. This data analysis has been attributed to Scatchard, and a plot of $\frac{V}{M_f}$ vs. V is termed a Scatchard plot (Stevenson, 1982; Tuschall, 1981). A theoretical Scatchard plot for titration of organic matter with metal is given in Figure 3-7. The illustrated approach suggests two categories of β, with one "strong" site and one "weak" site. Changes of β in aqueous humic-substance samples (SAPP 1) with different pH values were examined.

A potential problem with the equilibrium dialysis technique is the leakage of humic substances across the membrane. This would lead to an underestimation of the Pb binding capacity and conditional stability constants (Truitt and Weber, 1981a). Lowered accuracy

V = (metal complexed, M_C) / (total ligand, A_T)
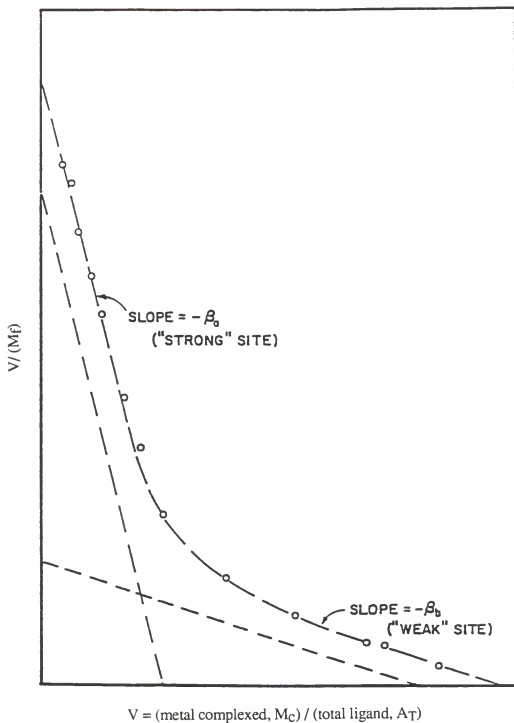
Figure 3-7. Theoretical Scatchard plot for conditional stability-constant determinations.

and reproducibility of analytical measurements further increased the uncertainty for metal binding capacities and determinations of stability constants (Haworth et al., 1987).

3.5 Systems Analysis

A system diagram of three alternative wetland management strategies is shown in Figure 3-8. These alternatives include planting, land control, and sediment excavation. Different strategies for wetland management should be able to attract resources from outside the region to promote the improvement of wetland function. An evaluation of the cost of these inputs can be performed in several ways. However, evaluation of wetland function improvement or benefit from nature is controversial. Systems analysis has proved to be a successful method for evaluating natural benefit. By estimating energy flows in terms of solar emergy (solar emjoules, sej), the cost of wetland management can be calculated with respect to macroeconomic value.

3.5.1 Emergy Analysis

In order to explain the energy analysis of a system, a common vocabulary and an understanding of certain fundamental ecological principles is needed (Odum, 1988a). The energy-language symbols initiated by Odum (1983) are helpful in explaining the wetland functions (Figure 3-9).

For an ecosystem, there is storage of biomass and energy at different trophic levels. Ecosystem processes occur when energy flows through each level. For the economic system, there can be storages of land, money, materials, etc., along with flows of energy, goods and services, etc. To interpret the relationship between the human economy and nature, the emergy or "solar energy equivalent" can be used as a common measure to express energy flow in an even more basic form. Some typical solar transformities used for emergy calculations are listed in Table 3-4.
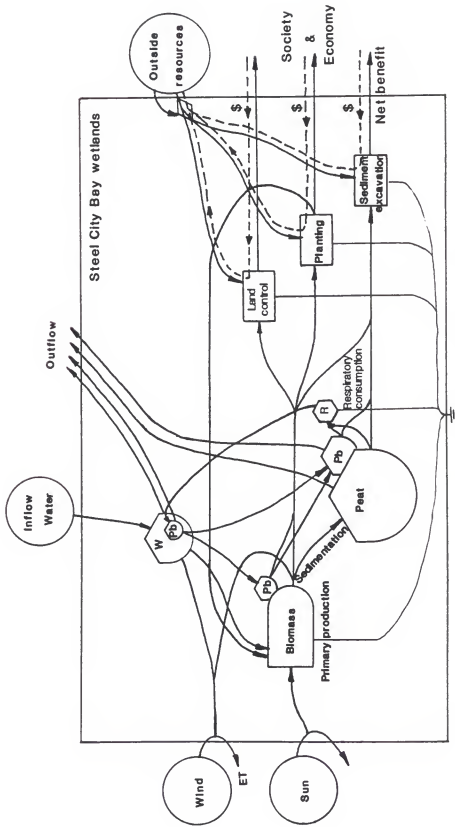
Figure 3-8. System diagram of three alternative wetland managements.

ENERGY PATHWAY - a flow of energy often with a flow of materials.

ENERGY SOURCE - energy which accompanies each of the resources used by the ecosystems such as sun, winds, tidal exchanges, waves on the beaches, rains, seeds brought in by wind and birds.

STORAGE TANK - a place where energy is stored. Examples are resources such as forest biomass, soil, organic matter, groundwater, and sands in beach dunes.

HEAT SINK - energy that is dispersed and no longer usable, such as the energy in sunlight after it is used in photosynthesis, or the metabolic heat passing out of animals. Heat sinks are attached to storage tanks, interactions, producers, consumers and switching symbols.

INTERACTION - process which combines different types of energy flows or flows of materials.

PRODUCER - unit which makes products from energy and raw materials, such as trees, grass, crops or factories.

CONSUMER - unit that uses the products from producers, like insects, cattle, micro-organisms, humans and cities.

TRANSACTION - business exchange of money for energy, materials or services.

SWITCH - process which turns on and off, such as starting and stopping fire, pollination of flowers, and closing of fishing season.

BOX - miscellaneous symbol for subsystems such as soil subsystems in a diagram of a forest, or a fishing business in a diagram of an estuary.

Figure 3-9. Symbols of energy circuit language, as used in emergy analysis. (After Odum, 1988a).

Table 3-4. Typical solar transformities (sej/j) used in emergy analysis.

Item	Solar transformities Solar emjoules/joule (sej/j)
Sunlight	1
1 Gross primary production	1091
Wind, kinetic energy	1496
Peat, organic matter	4420
Rain, geopotential	10488
Rain, chemical	18199
River, geopotential	27874
Runin (inflow)	41068
River, chemical	48459
Seedling production	120000
Fuel	18000 -- 100000
Human services	80000 -- 5000000000
Information	1E6 -- 1E32

Sources: Odum, 1991; Odum, 1993; Odum et al., 1987
1. Calculated for this study: Transformity = (Total solar emergy)/(Energy of primary production)

The following procedures were used for the emergy analysis of the Steel City Bay ecosystem:

1. Draw an energy system using the symbols of energy system language. This is an initial network overview to organize data-gathering efforts.

2. Collect data from various sources for the study area.

3. Prepare an emergy evaluation table:

    (a) List items of main flows from natural resources, imported sources, exports, and storages.

    (b) Derive raw data for the listed items. Data on energy or material inputs are usually expressed in energy units (J; joules), and human services in currency units ($; US $).

    (c) Evaluate listed flows and storages in emergy units (product of raw data and transformity) and macroeconomic values.

3.5.2 Emergy Evaluation

The environmental emergy contribution serves as an attraction for economic investments that bring in fuels, goods, services, technologies, etc., from outside. Purchased (society) inputs interact with the environmental (natural) resources in the ecological processes. The ratio of emergy brought into an area from the economy and the emergy of the environmental resources used in the interaction is the "emergy investment ratio" (Figure 3-10a). This index therefore is used to determine the economic competitiveness of an ecological process (Odum, 1993).

The net emergy, or emergy yield, of an ecological process is equal to the emergy of a source of energy minus the emergy used for processing (Odum, 1993). An ecological process also can be evaluated with the net emergy yield ratio, which is the ratio of the emergy yield divided by the emergy used for processing (Figure 3-10b). This index is useful for determining the benefit of an ecological process to society or the economy.
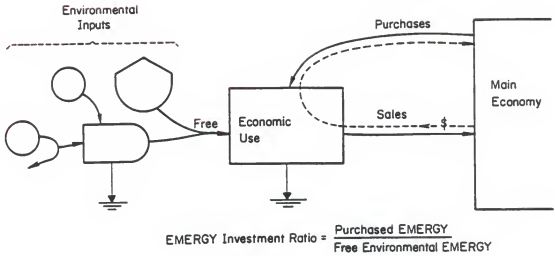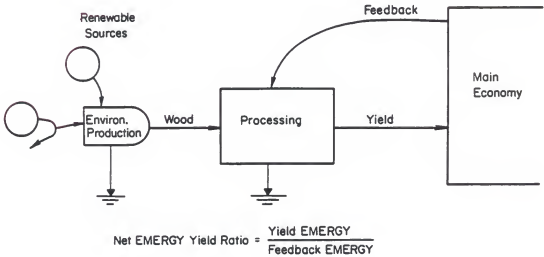
Figure 3-10. Emergy evaluation indices for evaluating an ecological process:
(a) Emergy investment ratio (b) Net emergy yield ratio
(After Odum, 1993)

The results of previous studies have shown the distribution of Pb in a wetland ecosystem (Ton, 1990; Ton et al, 1993). High percentages of stable forms of Pb in the wetland sediments suggested that the wetlands acted as a sink for the pollutants. The mobilization of a metal from sediments generally is an essential indicator of the potential hazards associated with that metal.

Lead can complex with organic ligands, followed by the adsorption of these complexes onto inorganic hydrous solids or organic particulates (Huang et al., 1977). These processes, complexation and adsorption, contribute to the high proportion of organically bound Pb, which was found to be the most abundant chemical form of Pb in soils and sediments (Davies, 1990; Ton, 1990). Hence, the stability of lead associated with organic compounds in the sediments is very important to characterize the potential hazards of Pb to wetland ecosystems.

Since Pb in dead plant tissues did not reach high levels in a previous study (Ton, 1990), it is reasonable to assume that there might have been other factors that resulted in the death of the vascular plants. The following studies, including a field study, a laboratory study and a microcosm study, were conducted to resolve this issue and also to understand the fate of Pb in this wetland ecosystem and to propose a practical wetland-management strategy to restore the damaged ecosystem.

4.1 Field Studies

Field conditions for the Steel City Bay wetlands were monitored routinely (approx. every 6 months) from April 1989 to September 1992. Sampling was designed to follow

the surface water drainage pattern. Sampling sites OF1 and OF2, Figure 3-2, were designated as the checkout points for the Steel City Bay and the end of study area, respectively. An open water cypress pond (i.e., site PC), which is isolated from the impacted surface water and is upgradient with respect to groundwater hydrology, was selected as the experimental control site.

The surface-water quality of the Steel City Bay wetlands is listed in Table 4-1. The distance is based on a reference from the discharge point at the Sapp Battery site, i.e., sampling site A. Results for the surface water samples indicate a trend of increasing pH, from 3.7 to 4.8, within the Steel City Bay despite the seasonal variations shown in Figure 4-1. This suggests that acid residuals at the Sapp Battery site still actively influence the adjoining wetlands. The same influence also can be observed in the electrical conductivity measurements, which decrease with increasing distance from the discharge area.

Low dissolved-oxygen contents (Table 4-1), less than 2.5 mg O_2/L, in most of the wetland areas indicated relatively high oxygen demand (biological or chemical) of the water column. Similar results of diurnal oxygen measurements made on August 21-22, 1990, are summarized in Appendix A. No oxygen levels exceeded saturation levels relative to the atmosphere, 0.15 to 3.38 mg O_2/L, with a low measurement at dawn and the highest value at sunset (Pritchard, 1992).

Oxygen is only sparingly soluble in water and diffuses about 10,000 times slower in water than in air (Reddy and Patrick, 1983; Schlesinger, 1991). Biological activity in aquatic systems and flooded soils often depletes oxygen within 36 hours after inundation (Reddy and Patrick, 1983). Nutrient analysis also suggests that the Steel City Bay wetlands serve as a sink for nutrients. Due to the depletion of oxygen in the water column, relatively high organic nitrogen and ammonia concentrations in surface water were attributed to the reducing environment.

Table 4-1. Water quality of the Steel City Bay wetlands in Jackson County, Florida (April, 1989 to May, 1992).

Item Sampling site*	A	B	C	F	D	OF1	G	OF2	E	H	PC
(n)**											
Distance (m)	0	240	444	459	587	600	900	1300	-	-	-
pH	3.7±0.4	4.1±0.4	4.1±0.4	4.5±0.6	4.5±0.3	4.8±0.9	4.5±0.4	4.3±0.4	4.6±0.6	5.1±0.5	5.6±1.2
Water depth (cm)	38±14	53±27	71±27	55±20	91±34	37±24	57±23	43±11	38±22	45±20	58±27
Electrical conductivity (S/cm-25°C)	171±116	56±27	45±17	44±13	28±3	33±6	56±32	44±21	46±18	48±18	39±9
Dissolved Oxygen (mg/L)	2.00	0.75	1.25	2.25	0.90	1.50	2.50	1.00	0.90	2.25	3.00
Nitrite + Nitrate (mg-N/L)	0.08	0.01	0.02	0.04	0.04	-	0.02	-	-	-	-
Ammonia (mg-N/L)	3.76	0.18	0.08	0.35	0.16	-	0.16	-	-	-	-
TKN (mg/L)	5.08	1.43	2.06	2.31	3.06	-	1.08	-	-	-	-
Total P (mg/L)	0.03	0.07	0.09	0.08	0.2	-	0.02	-	-	-	-
Total Pb (mg/L)	0.28-0.01	0.03-0.01	0.01-<.01	0.01-<.01	<.01	<.01	<.01	<.01	0.20-0.01	0.03-<.01	<.01

* See Figure 3-2 for locations of the sampling sites. Ordering of the sites is according to respective distance from discharge point A.

n - indicates no. of measurement.   - indicates no data available.

(mg/L=rpm)

** Single-valued parameters were measured in June of 1991 only.
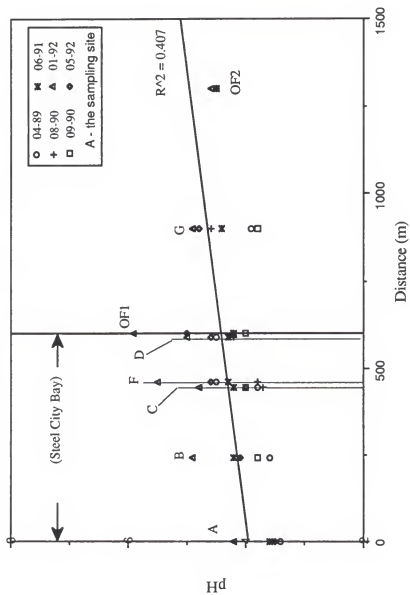
Figure 4-1. pH in surface waters of the Steel City Bay wetlands compared to distance from the discharge area.

Measurements of redox potential in aquatic systems are often closely related to the measurements of pH and dissolved oxygen (Stumm and Morgan, 1981). Variations of pH and redox potential in the water column for two sampling sites, B and C, were measured. Results of these measurements are shown in Figure 4-2. Reductions in redox potential with increasing water depth were observed at both sites. In contrast, pH values increased with increasing water depth.

Redox potentials versus pH values for surface water samples in Steel City Bay are shown in Figure 4-3. The diagram reveals a relatively close correlation ($r^2 = 0.705$) between redox potential and pH. This diagram was compared with the generic Eh-pH diagram (Figure 2-3, in section 2.5). According to this comparison, the surface water samples in the Steel City Bay reflect a reduced environment. Therefore, the reduction of redox potential in the water column can be referenced to decreasing dissolved-oxygen levels with depth. Under a reduced environment, due to the reduction of ferric oxides in the sediments which lowers the H^+ activity, pH should gradually increase in the water column with depth (Reddy and Patrick, 1983).

The surface-water flow rate varied with seasonal changes and storm events. Watts (1984) indicated that the flow discharge to Little Dry Creek was 2.83 L/sec (0.1 ft^3/sec) in May 1983. However, the creek may cease to flow on occasion. October and November generally are the driest months of the year (U.S. Soil Conservation Service, 1979). Low water levels were also observed during late April and May of 1991 and 1992.

A severe drought was in progress in May 1992, when the water level dropped to less than 30 cm in approximately one half of the Steel City Bay West, and in two-thirds of Steel City Bay East (Figure 4-4). In the adjacent wetland, only channelized water pools were present. Low rainfall was one of the reasons contributing to the drought, but farmers also continuously pumped out water for irrigation near site OF2. The exposed sediment in
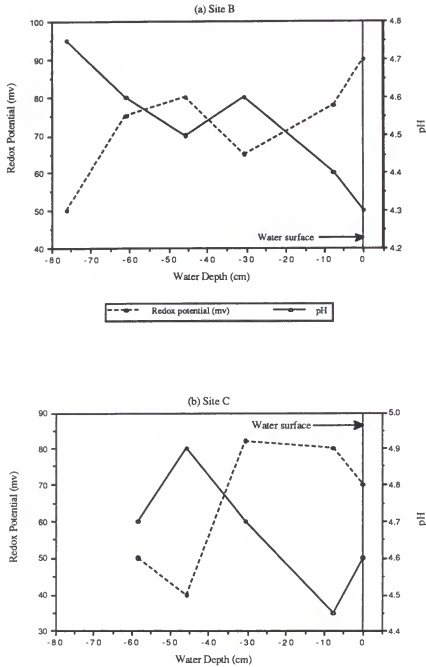
Figure 4-2. Variations of pH and redox potential with depth in the water column at Steel City Bay: (a) Site B (b) Site C.
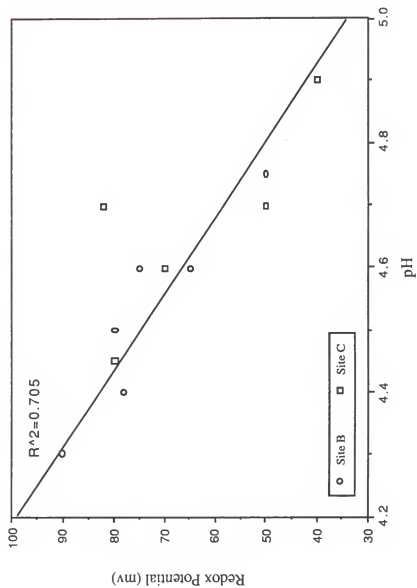
Figure 4-3. Redox potential vs. pH in surface water of the Steel City Bay.
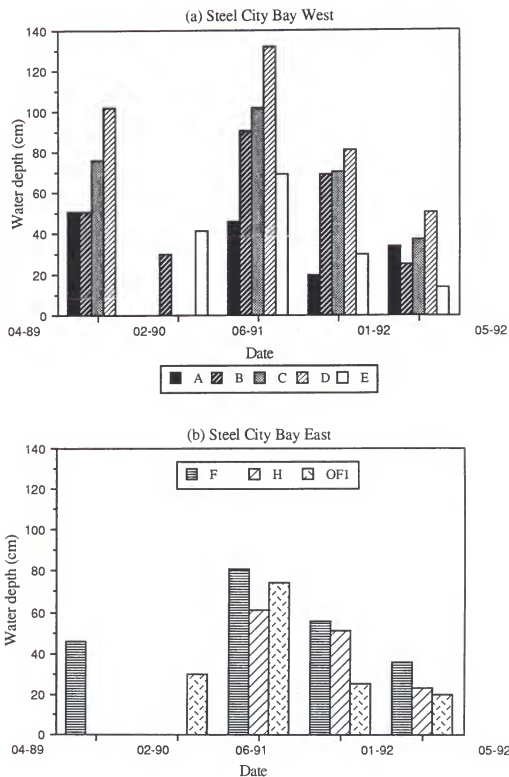
Figure 4-4. Hydrological fluctuations of surface water in the Steel City Bay wetlands from April, 1989 to September, 1992:
(a) Steel City Bay West (b) Steel City Bay East.

the highly elevated Pb-content area, site E, posed a potential risk of surface-water contamination due to the possibility of releasing Pb from oxidized organic matter.

The Sapp Battery environs are a unique location to study the biological processes of wetland community regeneration. This area was strongly impacted by the operation of Sapp Battery Service, Inc. Even though plant operation has ceased for more than a decade, acidity and Pb residuals still influence the adjoining wetland ecosystem.

East Swamp (Site A), which is located in the Sapp Battery site and receives discharges directly from the on-site property, was selected to observe the recovery of the wetland community under stress. Vegetation samples were collected and identified every 6 months from April 1989 to September 1992. The observed vegetation species are listed in Table 4-2. A dramatic increase in number of vegetation species was observed, ranging from 3 to 14, during the three years of field investigation. According to the empirical observation of the growing-area expansion and the quantitative estimation of population densities with respect to leaf area index of various species, an increase in biomass production was assumed as well (Pritchard, 1992).

4.1.1 Lead Concentrations in the Wetland Ecosystem

4.1.1.1 Surface water

Due to the mobility and bioavailability of Pb in the aqueous phase, Pb concentrations in surface waters may be used as an indicator of potential human-health risk. Total Pb concentrations in the surface waters from April 1989 to September 1992 are listed in Table 4-3. Site A, the wetland immediately adjacent to the Pb source, contained relatively high Pb concentrations. These averaged 0.13 mg/L with a standard deviation of 0.11. Most of the study area had Pb concentrations at or less than 0.01 mg/L. According to the surface water quality criteria for class III water (DER 17-320.560), the Pb concentration in the water for recreation, fish and wildlife should be less than or equal to 0.03 mg/L.

Table 4-2. Observed vegetation species in the East Swamp (site A) in Jackson County, Florida, from April, 1989 to September, 1992.

Species\ Date	*Before Jul-91	May-91	Sep-91
Woody species			
Taxodium ascendens			X
Herbaceous species			
Amphicarpus muhlenbergianum		X	
Astaraceae sp.			X
Cyperus distinctus		X	
Cyrilla racemiflora			X
Eleocharis baldwinii	X	X	X
Eleocharis equisetoides	X	X	X
Eleocharis vivipara		X	
Hypericum fasciculatum		X	X
Lachnanfles caroliniana			X
Ludwigia leptocarpa			X
Ludwigia pilosa		X	
Myrica cerifera			X
Nymphaea odorata	X	X	X
Rhexia alifanus			X
Scirpus cyperinus			X
Solidago fistalosa			X
Xyris sp.		X	X
Number of species	3	9	14

*Data cited from Pritchard, 1992.

Table 4-3. Lead concentrations in surface waters of the Steel City Bay wetlands, Jackson County, Florida.

*Site\ Date	Distance (m)	Apr-89	Feb-90	Aug-90	Jan-92	May-92	AVG	SD	MAX	MIN
		(mg/L)								
A	0	0.28	-	0.01	0.14	0.09	0.13	0.11	0.28	0.01
B	240	0.03	0.01	0.02	0.01	0.01	0.02	0.01	0.03	0.01
C	444	<.01	0.01	<.01	<.01	0.01	0.00	0.01	0.01	0.00
F	459	0.01	0.01	0.01	0.01	<.01	0.01	0.01	0.01	0.00
D	587	<.01	<.01	0.01	<.01	<.01	0.00	0.00	0.01	0.00
OF1	600	-	-	<.01	<.01	<.01	0.00	0.00	0.00	0.00
G	900	<.01	0.01	<.01	<.01	<.01	0.00	0.01	0.01	0.00
OF2	1300	-	-	<.01	<.01	<.01	0.00	0.00	0.00	0.00
E	-	-	-	0.01	0.20	0.06	0.09	0.10	0.20	0.01
H	-	-	0.03	0.01	<.01	<.01	0.01	0.01	0.03	0.00
PC	-	-	-	<.01	<.01	<.01	0.00	0.00	0.00	0.00

* See Figure 3-2 for location of the sampling sites. Ordering of the sites is according to respective distance from discharge point A.
AVG=Average. SD=Standard deviation. MAX=Maximum. MIN=Minimum. - indicates no data available.
Substitute 0.00 for <.01 in calculation of averages.
All data in this table are in units of mg/L (=ppm).

The results show a trend of decreasing Pb concentration in surface waters over time (Figure 4-5). It also shows a dramatic decrease of Pb concentration with increase in distance from the discharge area. The sediment-water interface is the principal medium for Pb removal. Removal of Pb from the water column by the organic-rich sediment through mechanisms such as sedimentation, adsorption, chelation, and precipitation has been reported elsewhere (Aiken et al., 1985; Chan et al., 1982; Florence and Batley, 1980; Huang et al., 1977; Ton, 1990).

Elevated Pb concentrations also were observed in the surface water samples at site E. Historical data indicated that site E was originally receiving wastewater from the service plant. Thus, elevated Pb concentrations in deposited sediments were considered to be the major cause of increased Pb concentrations of the surface water at both sites A and E.

A diagram of the distribution coefficient or partitioning coefficient, $Kd = ([Pb]$ in sediment)/([Pb] in water), suggested that high Pb concentrations of surface waters were correlated to elevated Pb concentrations in sediments (Figure 4-6). These incidents may also correspond with hydrological fluctuation of the surface water. A lowered surface water level during sample collection was postulated to be the possible effect, with the wetland sediments exposed to an oxidizing environment during the lower water level. Organically bound Pb may therefore have been released from oxidized organic matter, which contributed to increased Pb concentrations of the surface water.

4.1.1.2 Sediments

Total Pb concentrations in sediment samples are shown in Table 4-4. Comparison of these results with surface-water data (Table 4-3) indicates that most of the Pb is bound to sediments rather than remaining in the water column. A high concentration of Pb was observed in most of the sediment samples during 1989 and 1990. A remarkable decrease of Pb concentrations in the sediments of Site A, from as high as 400 μg/g to ca. 30 μg/g, was observed between January and May 1992. In an area relatively independent from

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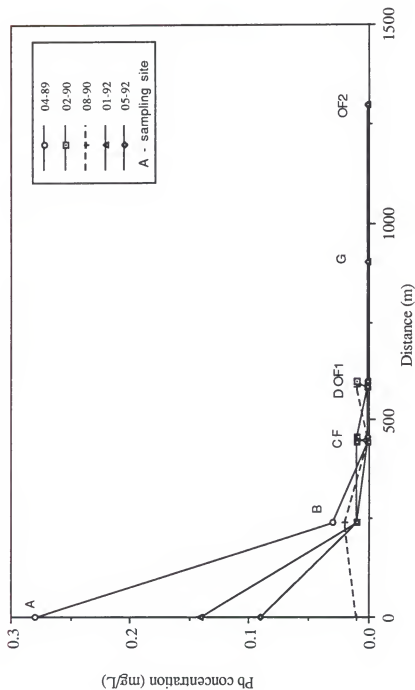
Figure 4-5. Lead concentrations in the surface waters of the Steel City Bay compared with distance from the discharge area.
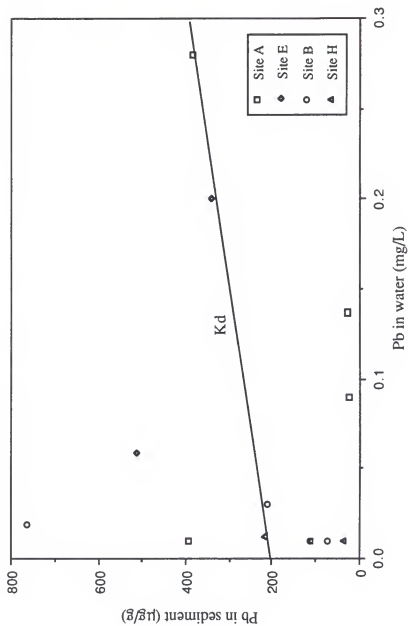
Figure 4-6. Distribution of Pb concentrations in surface waters and sediments.

Table 4-4. Lead concentrations in sediments of the Steel City Bay wetlands, Jackson County, Florida.

*Site\Date	Distance (m)	Apr-89	Feb-90	Aug-90	Jan-92	May-92	AVG	SD	MAX	MIN
		(µg/g)								
A	0	385.7	-	393.9	27.7	23.4	207.7	210.3	393.9	23.4
B	240	210.9	-	763.7	113.0	74.5	290.5	320.6	763.7	74.5
C	444	234.2	-	278.9	23.5	48.8	146.3	129.0	278.9	23.5
F	459	88.5	-	472.2	99.9	125.7	196.6	184.4	472.2	88.5
D	587	59.4	-	303.6	10.6	49.2	105.7	133.6	303.6	10.6
OF1	600	-	133.3	-	23.5	10.6	55.8	67.4	133.3	10.6
G	900	94.3	-	99.6	87.4	62.0	85.8	16.7	99.6	62.0
OF2	1300	-	-	-	10.6	10.6	10.6	0.1	10.6	10.6
E	-	-	477.8	-	342.1	512.0	444.0	89.8	512.0	342.1
H	-	-	-	215.7	36.3	112.9	121.6	90.0	215.7	36.3
PC	-	-	-	-	23.3	23.4	23.4	0.0	23.4	23.3

* See Figure 3-2 for location of the sampling sites. Ordering of the sites is according to respective distance from discharge point A.
AVG=Average. SD=Standard deviation. MAX=Maximum. MIN=Minimum.   - indicates no data available.
All data in this table are in units of µg/g (=rppm, dry weight).

surface water movement, site E, Pb contents of the sediments were less changed, with an average of 444.0 µg/g and a standard deviation of 89.8. At site G, the most remote area, concentrations in the sediments remained essentially constant, with an average of 85.8 µg/g and a standard deviation of only 16.7.

The gradient in Pb levels of the sediment compared with distance from the discharge area is shown in Figure 4-7. These results reveal that the distribution of Pb in sediment corresponds with the surface-water drainage pattern. Relatively low Pb concentrations outside the boundary of the Steel City Bay, i.e., OF1, suggest that the wetland acts as a filter to retain Pb.

In general, high concentrations of metal pollutants are usually discovered in the top layer of the river sediments (Garlaschi et al., 1985). Vertical profile data for Pb in sediment/soil samples were reported earlier (Ton, 1990). The distribution of Pb in the soil/sediment profiles indicated that most of the Pb was accumulated in the top layer of soil and sediment, i.e. the 0 to 15 cm depth.

The majority of waterborne pollutants such as metal ions can adsorb onto particulate matter or form complexes with organic and inorganic ligands and settle down to the sediment layers (Aiken et al., 1985; Chan et al., 1982; Florence and Batley, 1980; Huang et al., 1977; Nixon and Lee, 1986). Sedimentation, adsorption, chelation, and precipitation apparently scrub the water column effectively, and prevent dispersal of the pollutants.

Soil and sediments also have been proven to have rather large capacities for the immobilization of Pb. The organic fraction is largely responsible for the observed fixation of Pb remaining near the soil surface (Davies, 1990; Ton. 1990; Ton et al., 1993). The organic-rich sediments in the study area are further bound in place by plant roots. The tendency for these sediments to become anaerobic under flooded condition probably is the major factor involved in the retention of Pb (Chan et al., 1982). Reducing environments
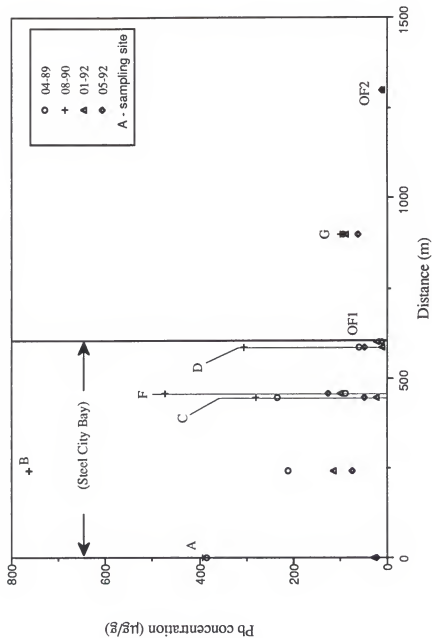
Figure 4-7. Lead concentrations in sediment of the Steel City Bay wetlands compared with distance from the discharge area.

also allow the conversion of heavy metals into relatively insoluble sulfides due to the reduction of sulfates (Alloway, 1990; Brookins, 1988; Kelly, 1988; Nriagu, 1978a).

An expanded growing area and increased population densities of eel grass (*Eleocharis* sp.) and other emergent aquatic plants apparently increased biomass production at site A. Because of the evolution of plant adaptation, high above-ground biomass and net annual primary productivity of similar aquatic species were reported earlier (Bradbury and Grace, 1983; Chan et al., 1982; Nixon and Lee, 1986) which also suggested the possibility of increasing sediment accumulation. Sediment samples were taken only from the top layer of the soil/sediment profile, 0 to 15 cm. Dilution by deposition of newly degraded plant material is reasonable to explain the dramatic decrease in Pb concentrations of the sediments at site A.

Thick populations of emerged aquatic plants (*Nymphaea odorata*) throughout the study area (Pritchard, 1992) also could affect the Pb concentrations in sediments. Due to the relatively high turnover rate of these aquatic species, freshly degraded biomass covered the bottom of the wetland and diluted Pb concentrations in the sediment.

Moreover, erosion of the railroad base could be another possibility for decreasing the Pb contents of the sediment samples. An increased clay content at sites C and D was observed during sample collections in 1992. Comparison of dry sediment samples from earlier collections, with a change of color from dark brown to bright yellow, further suggested changes in clay content. However, considerable spatial heterogeneity throughout the study area may have contributed to the dramatic change in apparent Pb levels of sediment samples for different sampling events (Ton et al., 1993).

4.1.1.3 Vegetation

During the field study, water lily (*Nymphaea odorata*) was the predominant species for the entire wetland, excluding site A. A systematic investigation of this aquatic plant thus was necessary to understand the correlation between Pb and vegetation. Leaves, stems, and roots of water lily were separated for Pb analysis. The combination of leaves

and stems was termed "above-ground biomass." Roots then represented "below-ground biomass."

Data for total Pb concentrations in *Nymphaea odorata* are shown in Table 4-5. Due to the difficulty in accessing site A during earlier field trips, no *Nymphaea odorata* samples were collected until the last trip (May of 1992). Lead concentrations in most of the below-ground biomass were close to the instrumental detection limit, i.e., 10.0 µg/g. Concentrations of Pb in above-ground biomass (*Nymphaea odorata*) were slightly higher. In areas with elevated Pb levels in water and sediments (sites A and E), the differences in Pb concentrations between above-ground and below-ground biomass became larger. However, high concentrations of Pb accumulated in below-ground biomass were observed for other species, such as *Juncus* sp., *Eleocharis* sp., *Hypericum fasciculatum*, *Ludwigia* sp., and *Xyris* sp. Results of the other vegetation analyses are included in Appendix B.

Relationship of Pb concentration in *Nymphaea odorata* with distance from the pollutant source is shown in Figure 4-8. Similar patterns of Pb accumulation in above-ground and below-ground biomass of *Nymphaea odorata* along the drainage pathway were found. Results suggest that the accumulation of Pb in *Nymphaea odorata* are related to the gradient in Pb levels of the surface-waters and sediments.

Vegetation was considered to increase the overall capacity of a wetland ecosystem to retain or remove pollutants such as Pb through interactions with various anaerobic and aerobic soil layers and water interfaces. In particular, uptake by plant root of pollutants from the sediment could free more exchange sites in the sediments for further pollutant interaction and accumulation (Chan et al., 1982).

Metal pollutants in the ionic form can be actively taken up by vegetation and accumulated in concentrations in excess of their ambient levels (Chan et al., 1982, Kelly, 1988; Stumm and Morgan, 1981). Processes of metal uptake in vegetation systems can be summarized as:

1. uptake through the plant-soil interface, via below-ground biomass;

Table 4-5. Lead concentrations in vegetation from the Steel City Bay wetlands, Jackson County, Florida.

Date/Sampling site*	(Item)§	A	B	C	F	D	OF1	G	OF2	E	H	PC
Nymphaea odorata												
Apr-89	AG	-	75.0	12.5	12.5	12.5	-	-	-	-	-	-
	BG	-	62.5	12.5	50.0	-	-	-	-	-	-	-
Aug-90	AG 1	-	23.3	23.0	48.7	10.6	-	10.6	-	-	-	-
	AG 2	-	10.6	10.5	49.0	10.5	-	23.1	-	-	-	-
	BG 3	-	61.6	10.6	23.2	10.4	-	10.5	-	-	-	-
Jan-92	AG 1	-	73.7	23.5	10.6	10.5	23.5	36.1	-	18.4	-	10.6
	AG 2	-	74.5	23.4	10.6	10.5	10.6	10.6	-	252.6	-	10.5
	BG 3	-	23.5	23.4	10.6	10.6	10.6	10.6	-	183.5	-	10.5
May-92	AG 1	369.5	23.5	23.4	36.1	10.6	10.6	10.6	<10.0	203.1	<10.0	<10.0
	AG 2	341.8	10.6	10.6	10.5	10.6	10.6	<10.0	10.6	151.3	10.6	<10.0
	BG 3	23.3	10.5	<10.0	10.6	<10.0	10.6	10.6	<10.0	317.6	<10.0	<10.0

*See Figure 3-2 for locations of the sampling sites. Ordering of the sites is according to respective distance from discharge point A.
§Item AG- above-ground biomass, BG- below-ground biomass, AG- (1-leaves, 2-stems), BG- (3-roots). - indicates no data available.
All data in this table are in units of μg/g (=rppm, dry weight)
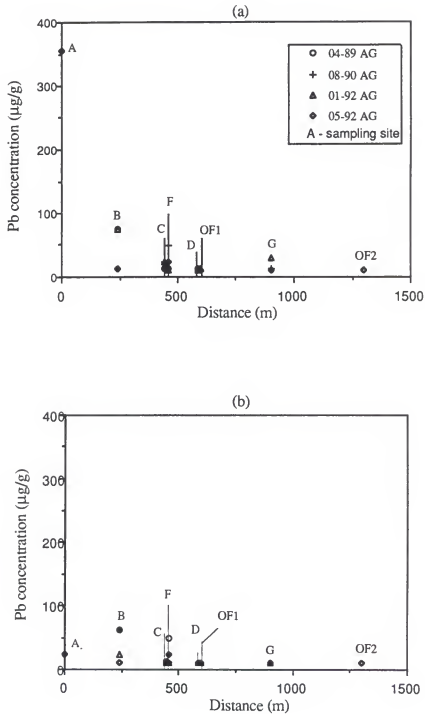
Figure 4-8. Lead concentrations in vegetation (*Nymphaea odorata*) of the Steel City Bay
compared with distance from the discharge area:
(a) Above-ground biomass (b) Below-ground biomass.

2. uptake through the plant-water interface, via above-ground biomass;

3. translocation through the vascular system of plants, from below-ground biomass to above-ground biomass during the growing season; and

4. adsorption and immobilization by the plant (Alloway, 1990; Chan et al., 1982; Kelly, 1988; Nixon and Lee, 1986; Nriagu, 1978b).

The primary uptake would be through below-ground biomass at the plant-soil interface. Uptake capability usually is directly proportional to the volume of below-ground biomass except in some submerged and floating species, which have poor root systems (Chan et al., 1982). Therefore, the plants having higher Pb uptake (Appendix B) are generally shallow-rooted, and are exposed to the higher concentrations of Pb that accumulated in the upper soil/sediment layer. However, emergent plant species (*Nymphaea odorata*) also are capable of absorbing metals through their above-ground biomass. In some fast-growing species such as *Eleocharis* sp. and *Juncus* sp., uptake of Pb increases with increasing Pb concentration in the water and sediments. In this study, the highest level of Pb was found in the below-ground biomass of *Juncus* sp., 2068 µg/g.

4.1.1.4 Quality assurance and quality control

To insure the validity of the data, a QA/QC program was employed. The program for this study included analysis of EPA QC samples in every analysis series. The recoveries of standard spikes in 10% of water samples and solid-sample digestates (sediment and vegetation) also were checked. Results for the analysis of EPA water and sediment evaluation samples were within the acceptable range, i.e., true value ± 95% confidence interval. The results for duplicate samples and spike recoveries were also within the 95% confidence interval in the water samples and within the 90% confidence interval for the sediment and vegetation samples.

4.1.2 Bioconcentration Factors

      The accumulation of Pb over time in vegetative tissues was observed for several species during the field study. *Nymphaea odorata* is the only vegetation species which has sufficient data to characterize the mechanism of bioconcentration. Vegetation was divided into two major parts; above-ground and below-ground biomass. To understand the correlation of bioconcentration with ambient environments, the concentration of Pb in each portion of each vegetative sample was compared to the concentrations of Pb in surface waters and sediments.

      The accumulation of Pb from the ambient environment by above-ground and below-ground biomass of *Nymphaea odorata* is shown in Figure 4-9. According to the curve fitting function of the computer program, the data indicate a correlation between Pb in above-ground biomass with Pb in surface water, for which the r^2 was equal to 0.960 and 0.734 for the spring season and fall season, respectively (Figure 4-9a). The correlation of Pb in below-ground biomass with Pb in water is illustrated in Figure 4-9b. A high correlation ($r^2 = 0.942$) for the fall season and no correlation ($r^2 = 0.265$) for the spring season were observed for below-ground biomass with Pb in surface water. No correlation was observed between Pb in above-ground biomass and Pb in sediment for either the spring, $r^2 = 0.059$, or fall, $r^2 = 0.041$, seasons (Figure 4-9c). A moderate correlation ($r^2 = 0.782$) between Pb in below-ground biomass and Pb in the sediments was obtained for the spring season, but no correlation was found for the fall season, $r^2 = 0.179$ (Figure 4-9d).

      Such results may suggest that in the spring (growing) season the mechanism for Pb uptake is from its ambient environment, e.g., above-ground biomass uptake of Pb from the surface water as well as below-ground biomass uptake of Pb from the sediment. Movement of pollutants through the vascular system of a plant can increase the capability for absorbing Pb (Påhlsson, 1989). During the growing season, translocation of nutrients from below-ground biomass to above-ground biomass usually increases the uptake of metals and enhances metal concentrations in above-ground biomass (Chan et al., 1982).
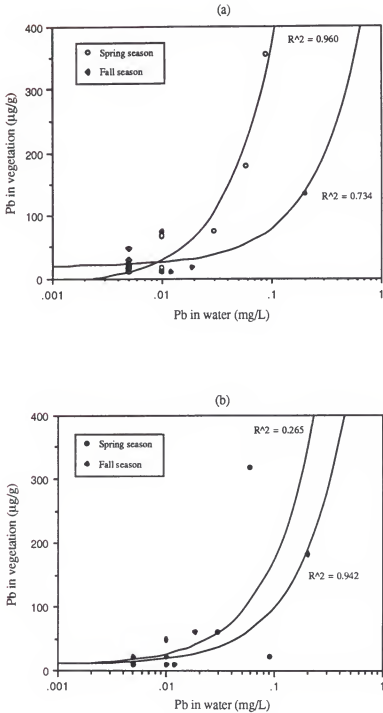
Figure 4-9. Accumulation of Pb from water and sediment by the above-ground (AG) and
below-ground (BG) biomass of <u>Nymphaea odorata</u>:
(a) <u>Nymphaea od.</u>- AG vs. water (b) <u>Nymphaea od.</u>- BG vs. water
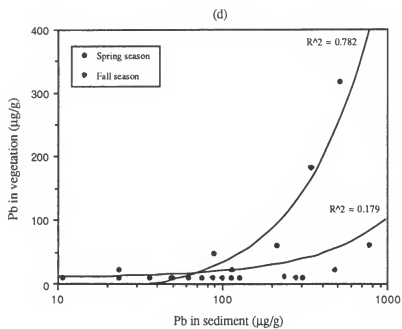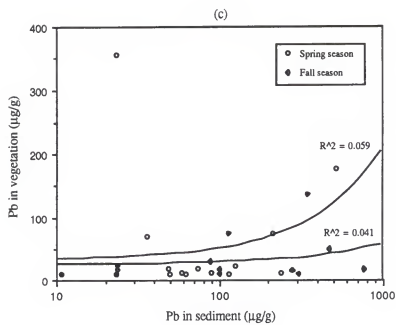
Figure 4-9. Continued
(c) <u>Nymphaea od.</u>- AG vs. sediment (d) <u>Nymphaea od.</u>- BG vs. sediment.

However, differences in uptake characteristics by tolerant and nontolerant genotypes may be manifestations of metal uptake as well (Shaw, 1989).

In a nongrowing season (the fall), translocation of Pb from above-ground biomass to below-ground biomass may contribute to a higher correlation between Pb in surface water and Pb in below-ground biomass, although Alloway (1990) and Davies (1990) suggested that Pb was translocated only slightly. Peterson (1978) also suggested that the Pb content of vegetation is largely dependent upon plant growth rate. During periods of active growth, despite the plants are constantly uptaking Pb, a decrease in Pb concentration may be expected. Low Pb levels in *Nymphaea odorata* suggest the possibility of a dilution factor due to biomass production

According to the studies of Pb accumulation by the different species, sediment is likely the most important ambient environment for Pb enrichment in vegetation. The bioconcentration factor (BCF) therefore is defined as

$$BCF = \frac{\text{concentration in BG vegetation}}{\text{concentration in sediment}}$$

The BCFs for 13 different vegetation samples are listed in Table 4-6. Samples from two dead woody species (*Taxodium ascendens* and *Nyssa sylvatica*) were taken in the first field trip (April of 1989). *Nymphaea odorata* samples were obtained throughout the entire study area. Algae samples were collected from the Steel City Bay East. The rest of the species were collected from either site A or site E (locations of the higher Pb levels in surface water and sediments), to study bioconcentration factors.

Taxodium ascendens, Nyssa sylvatica, and *Nymphaea odorata* showed smaller BCF values, averaging 0.3, 0.4, and 0.3, respectively. For all other species, the below-ground biomass gave a higher BCF value. The highest BCF among them was 41 for the below-ground biomass of *Hypericum fasciculatum*, although the BCF value tended to decrease as the sediment concentration increased (Figure 4-10). This presumably

Table 4-6. Bioconcentration factors for vegetation of the Steel City Bay wetlands in Jackson County, Florida

Species		Apr-89	Feb-90	Aug-91	Jan-92	May-92	Mean
Woody species							
Taxodium ascendens			0.3				0.3
Nyssa sylvatica			0.4				0.4
Herbaceous species							
Algae			1.7				3.4	2.5
Amphicarpus muhlenbergianum	AG					1.5	1.5
	BG					5.4	5.4
Cyperus sp.	AG					0.4	0.4
	BG					7.5	7.5
Eleocharis baldwinii	AG			1.7	8.7	7.0	5.8
	BG			1.6	21.7	32.6	18.6
Eleocharis equisetoides	AG			0.2	1.3	0.4	0.6
	BG			1.9	3.1	6.5	3.8
Hypericum fasciculatum	AG					0.5	0.5
	BG					41.0	41.0
Juncus sp.	AG		1.8		0.6	0.8	1.0
	BG		3.6		3.6	4.0	3.8
Ludwigia sp.	AG					3.7	3.7
	BG					19.0	19.0
Nymphaea odorata	AG	0.2		0.1	0.5	0.4	0.3
	BG	0.3		0.1	0.4	0.5	0.3
Xyris sp.	AG					11.4	11.4
	BG					25.0	25.0

AG- above-ground biomass, BG- below-ground biomass.

Bioconcentration factor is defined as: $\dfrac{\text{Pb in vegetation}}{\text{Pb in sediment}}$

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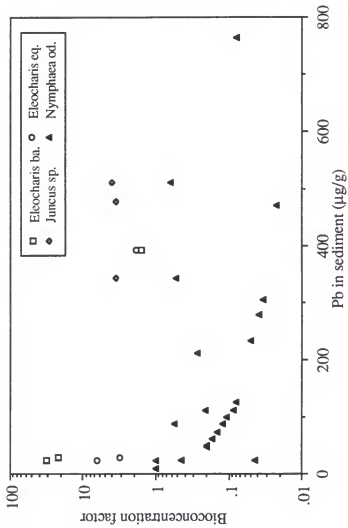
Figure 4-10. Bioconcentration factors for Pb in vegetations.

represents the decreased availability of sites to bind metals as the concentration increases (Kelly, 1988). These may use exclusion as a Pb tolerance mechanism.

The BCF evaluation also reflects the influence of pH. The vegetation samples with higher values of BCF were collected from site A and E, which usually had the lowest pH in the study area. Thus, low pH may increases the bioavailability of Pb in sediments and enhance the BCF for below-ground vegetation biomass. Similar relationships for bioconcentration factor and pH also were reported earlier (Kelly, 1988).

A global model of the Pb cycle consists of certain reservoirs among which transfer of Pb may occur (Table 2-6). As a common practice in biogeochemistry, it is assumed that the material cycled and utilized within the system is at steady state. The carrying capacity, which is defined as the maximum number of individuals that can persist under the specified conditions, also can be expressed as the ability of a system to assimilate waste and residuals in environmental studies (Colinvaux, 1986, Nriagu, 1978a, 1978b). Therefore, "environmental pollution" is identified when the assimilation capacity of any component at any level is exceeded. As a result, the productivity and established dynamics of the ecosystem are affected by an excess of man-made materials (Nriagu, 1978a).

The biogeochemical cycle of Pb in a wetland ecosystem suggests that Pb tends to accumulate in the compartment which has the longest residence time. The mean residence time for Pb in organic-rich wetland sediment has been estimated to be as long as one million years (Schlesinger, 1991). The turnover time of Pb in living biota has been estimated to be 51 years (Nriagu, 1978a). Therefore, organic-rich soils generally have high Pb concentrations, and the living biotic pool also may be considered as another terrestrial Pb reservoir (Nriagu, 1978a).

4.2 Microcosm Study

Destruction of the biological community of the on-site wetlands and the Steel City Bay wetlands is strong evidence of ecotoxicity to the wetlands ecosystem. This

phenomenon also alerted the public about pollution in the environment. Earlier, very low pH values and elevated concentrations of Pb were reported in discharges from the battery reclamation plant, i.e., as low as 1.2 for surface-water pH and 3.78 mg/L for the Pb concentration (Watts, 1984). moderate pH values ranged from 3.2 to 4.5 in subsequent studies also revealed the influence of residuals from previous discharges to the downstream wetlands (CH$_2$M HILL, Inc., 1991; Ecology and Environment, Inc., 1986; Mundrink, 1989; Ton, 1990; Ton et al., 1993; Trnovsky et al., 1988).

Results of the current studies suggested that most Pb is bound to the sediment, and that only a trace amount of Pb remains in the water column, i.e., ≤ 0.01 mg/L. The pH in the study area is lower than for the normal aqueous environment, but close to that for the organic-rich wetland surface waters, ranging from 3.7 to 5.1 (Table 4-1).

It has been postulated that a high concentration of Pb in the growing medium and/or low pH values in the surrounding water are the major factors affecting growth of wetland species. However, according to a toxicity study for Pb using vascular plants (Påhlsson, 1989), the concentration of Pb in dead plant tissue from the earlier report was not considered high enough to cause devastation of the wetland community (Ton, 1990). To determine the causes of such devastation, microcosms were established to examine the toxicity of Pb and the tolerance to acidity of the wetland species.

Pond cypress and black gum seedlings were planted in a sediment mixture similar to that found under field conditions. In order to have a simplified natural ecosystem that maintained a level of complexity, "self-organization" was employed by "seeding" a field sediment sample (site PC) into individual testing units (Odum, 1988b). As a result, each test unit consisted of a diversity of vegetation species similar to that of a natural system, i.e., *Eleocharis* sp. and *Nymphaea odorata* .

A period of two months was designated for the stabilization of seedlings and the development of self-organization in the microcosms before any measurements were taken. The height of the seedlings was monitored and the growth rates were calculated.

Comparison of the average growth in height of pond cypress and black gum seedlings in the microcosms was obtained, with the results being shown in Figure 4-11.

The solid line represents the growth curve for seedlings of pond cypress, and the dashed line shows the growth rate for seedlings of black gum. In general, the increase in height of pond cypress seedlings is greater than that for black gum seedlings (Deghi, 1984). In the first eight months, the growth rate curves were smooth, with a plateau during the dormant seasons. A rapid growth of the seedlings in the microcosms was then observed after dormancy. Sufficient nutrients in the substratum, due to the addition of fertilizer before replanting and without further dispersal from the planting pot, is a possible explanation for the enhanced growth in the microcosms.

Chemical treatments, i.e., acidic water and Pb solutions, were applied to the microcosms after the first dormancy. Under a standard set of experimental conditions (section 3.3.1), the various effects of chemical treatments on the growth of the seedlings were obtained. The mean growth rate of the seedlings in each treatment combination is shown in Table 4-7. Due to some unexpected biological activity in the distribution system, the actual values of the chemical reagents did not reach the nominal (expected) values, although they reflected field conditions to some extent. The results revealed a variation in the mean growth rate of pond cypress seedlings. The mean growth rate of black gum seedlings was less changed than that of pond cypress, despite the varying chemical treatments.

To analyze growth response from the various treatments, statistical analyses were employed. Analyses of variance (ANOVA) for the growth of cypress and black gum are shown in Table 4-8 and Table 4-9, respectively. Three levels of acid and Pb were added as treatments; therefore, each chemical addition has two degrees of freedom, while the treatment combinations have four degrees of freedom. Eight measurements, each reflected as an average of six duplicated samples, of seedling growth in each treatment combination were obtained. As a result, the total degrees of freedom were 71, i.e., $8*3^2 - 1=71$.
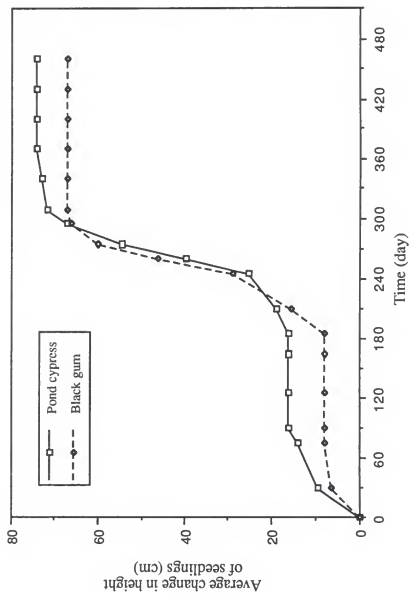
Figure 4-11. Average growth in height of pond cypress and black gum seedlings.

Table 4-7. Effects of chemical treatment on the growth of pond cypress
(*Taxodium ascendens*) and black gum (*Nyssa sylvatica*) seedlings.

Treatment	(n)	Chemical reagent				Test Species			
		Pb		Acidity (pH)		*Nyssa sylvatica*		*Taxodium ascendens*	
		nominal (mg/L)	actual	nominal	actual	mean growth cm/month		mean growth cm/month	
3	8	4.88	1.52	6.4	5.4	8.13	r^2=0.997	4.70	r^2=0.984
8	8	4.88	2.35	2.4	4.3	7.33	r^2=0.984	6.22	r^2=0.993
9	8	4.88	2.32	4.5	5.6	8.19	r^2=0.996	6.73	r^2=0.984
2	8	0.44	0.13	6.4	5.6	6.99	r^2=0.996	6.64	r^2=0.986
6	8	0.44	0.30	2.4	4.7	7.59	r^2=0.999	5.71	r^2=0.983
7	8	0.44	0.23	4.5	5.7	7.43	r^2=0.995	4.22	r^2=0.991
1	8	0	0	6.4	5.7	8.16	r^2=0.996	7.37	r^2=0.985
4	8	0	0	2.4	4.4	7.91	r^2=0.994	6.89	r^2=0.981
5	8	0	0	4.5	5.4	7.81	r^2=0.999	7.11	r^2=0.987
control	8	0	0	6.4	6.4	7.89		6.99	

n- indicates numbers of collected data

Table 4-8. The ANOVA (analysis of variance) for growth of *Nyssa sylvatica* with chemical treatments.

Factor	Type	Levels	Values		
Acid	Fixed	3	1	2	3
Pb	Fixed	3	1	2	3

Analysis of Variance for growth

Source	DF	SS	MS	F	P
Acid	2	0.52	0.26	0.00	0.996
Pb	2	5.59	2.79	0.05	0.955
Acid x Pb	4	5.22	1.30	0.02	0.999
Error	63	3785.41	60.09		
Total	71	3796.73			

DF-degrees of freedom, SS-sum of squares, MS-mean square.
F-test with denominator: Error
Denominator MS = 60.09 with 63 degrees of freedom
($\alpha = 0.05$)

Table 4-9. The ANOVA (analysis of variance) for growth of *Taxodium ascendens* with chemical treatments.

Factor	Type	Levels	Values		
Acid	Fixed	3	1	2	3
Pb	Fixed	3	1	2	3

Analysis of Variance for growth

Source	DF	SS	MS	F	P
Acid	2	0.89	0.44	0.02	0.983
Pb	2	33.73	16.87	0.65	0.524
Acid x Pb	4	41.64	10.41	0.40	0.806
Error	63	1627.97	25.84		
Total	71	1704.23			

F-test with denominator: Error
Denominator MS = 25.84 with 63 degrees of freedom
($\alpha = 0.05$)

The hypothesis of this statistical analysis was that the acidity and Pb had significant effects on the growth of pond cypress and black gum seedlings. An F-test was performed for hypothesis testing. With error as the denominator and treatment as the numerator, the ratio of F_0 is defined as

$$F_0 = \frac{MS_{Treatment}}{MS_{Error}}$$

An F-distribution, $F_{.05,\ 2,71} = 3.07$, is obtained from the reference table to test the null hypothesis (Montgomery, 1984). The values of F_0 for each treatment are very small and less than $F_{.05,\ 2,71}$. Therefore, the null hypothesis cannot be rejected. This means there were no significant effects of acidity and Pb on the growth of seedlings of either species.

Analysis of the difference between species was performed in the same manner. Results of this analysis of variance are shown in Table 4-10. The F-test reveals that there was no significant difference in growth between species.

Comparing treatments with a control to determine the difference among treatments is commonly performed (Montgomery, 1984). The results of such testing revealed a strong correlation between treatments and the control, with R squared ranging from 0.999 to 0.984 and 0.993 to 0.981 for black gum and pond cypress, respectively (Table 4-7).

In conclusion, for the microcosm study under simulated current field conditions, neither the pH nor the Pb concentration had any significant effect on the growth of seedlings. However, the difference of the mean growth rates of the seedlings among treatments showed that Pb concentrations in the water had greater influence on the growth of pond cypress seedlings than on that of black gum. This evidence suggests that pond cypress is more sensitive to chemical stress. Such findings may also explain the recovery of the black gum community, though not pond cypress, in the Steel City Bay wetlands after the battery-acid devastation.

Table 4-10. The ANOVA (analysis of variance) for growth of *Nyssa sylvatica* and
Taxodium ascendens with chemical treatments.

Factor	Type	Levels	Values		
Species	Fixed	2	1	2	
Acid	Fixed	3	1	2	3
Pb	Fixed	3	1	2	3

Analysis of Variance for growth

Source	DF	SS	MS	F	P
Species	1	86.34	86.34	2.01	0.159
Acid	2	0.16	0.08	0.00	0.998
Pb	2	29.96	14.98	0.35	0.706
Species x Acid	2	1.25	0.63	0.01	0.986
Species x Pb	2	9.36	4.68	0.11	0.987
Acid x Pb	4	19.05	4.76	0.11	0.979
Species x Acid x Pb	4	27.81	6.95	0.16	0.957
Error	63	5413.38	42.96		
Total	71	5587.31			

F-test with denominator: Error
Denominator MS = 42.96 with 126 degrees of freedom
($\alpha = 0.05$)

4.3 Laboratory Study

Organically bound Pb was found to be the most abundant chemical form of Pb in sediments (Ton, 1990). Hence, the stability of lead associated with organic compounds in the sediment is very important when characterizing the potential hazards of Pb to wetland ecosystems. The behavior of trace metals in aquatic systems is highly complex, due to the number of interactions and various external-factor changes including pH, redox potential, and concentrations of interacting substances. To understand the response of organo-Pb complexes under different environmental conditions, a laboratory study was conducted to determine their stability constants.

Due to the strong influence of residual acid on the pH of surface water from the study area, pH was selected as a variable for this study. Three different pH values, 3, 5, and 7, were used to examine stabilities of the complexes of Pb between aquatic humic substances. Aquatic humic substances (SAPP1), isolated from the surface water of site PC, were used to examine the complexation behavior. For comparison, a commercial humic acid [Aldrich humic acid (AHA), a product of Aldrich Chemical Co.], purified and freeze dried by Davis (1993) was used.

Since the method introduced for this dialysis analysis was being used for the first time, characterization of the materials and their performance was also addressed. A blank test, involving electrolyte dialysis against an electrolyte, was used for the determination of equilibrium time. The equilibrium time for Pb ions was obtained by detecting the approach to equilibrium concentration from both directions during dialysis. Equilibrium was obtained within 4 hours following the addition of 1.0 ml of Pb^{2+} standard-solution (Figure 3-6a). After the addition of another 0.5 ml of Pb^{2+} standard-solution, equilibrium was reached again in less than 4 hours (Figure 3-6b). Thus, 6 hours and 12 hours were presumed to be sufficient to reach equilibrium for the 0.5 mL and 1.0 mL Pb standard additions, respectively.

The mass balance for Pb concentrations from both directions was also calculated. The percentages of Pb adsorbed onto the hollow fibers was less than 0.5% at the equilibrium concentration of 1 mg/L, with an increase to 1.9% when the equilibrium concentration reached 6 mg/L. Ultraviolet/visible adsorption spectroscopy at wavelength λ = 345 nm was used to determine the concentrations of organic matter passed through the fiber membranes. A mass-balance calculation showed that the permeation rate for AHA averaged less than 1%, with only 0.07 mg of organic permeating through membrane. Permeation percentages for the SAPP1 sample were higher and ranged from 2.9% to 6.2% for pH=7 to pH=3, respectively. The mass of aquatic organic matter that permeated the membrane was 0.29, 0.57, and 0.62 mg for pH= 7, 5, and 3, respectively.

Low-molecular-size fractions, i.e., 1,000 to 10,000 Daltons, usually predominate for the aquatic fulvic acids, while commercial humic acid (AHA) consisted of relatively high-molecular-size fractions, i.e., $\geq$ 50,000 D (Alloway, 1990; Summers et al., 1987). The ionic strength as well as pH effects on molecular size distribution of humic substances has been reported elsewhere (Cornel et al., 1986; Ghosh and Schnitzer, 1980; Summers et al., 1987). Results of these studies suggest that humic substances assume a more extended configuration at low-ionic strength and higher pH, i.e., $\geq$ 3.5, and therefore may be rejected at the membrane surface due to size exclusion. On the other hand, high ionic strength and low pH tend to protonate the carboxylic groups on the organic matter, thereby causing the organic molecule to become less extended in solution and allows more molecules to permeate the membrane. This is postulated as the reason for the increased organic permeation of SAPP1 with decreasing pH.

4.3.1 Lead Binding Capacity for Humic Substances

The Pb binding capacities of AHA were determined by plotting the freely dissolved Pb concentration, M_f, versus the total Pb concentration, M_t. A linear portion of the curve

was obtained and that portion was extrapolated to the abscissa to determine the Pb binding capacity (Davis, 1993; Truitt and Weber, 1981a).

The diagram for Pb bound to AHA are shown in Figure 4-12. The Pb binding capacity of AHA was determined as the interception of M_t. The value was converted to mole concentration by divided by molecular weight of Pb. Since 20 mg of humic substances were used to prepare organic sample, 10 mg (50% of the humic substances) were assumed to be organic carbon (Stevenson, 1982). Therefore, the Pb binding capacities of AHA were calculated to be 3.24E-2 μM Pb/mg C and 3.45E-2 μM Pb/mg C at pH 3 and 7, respectively. Figure 4-13 similarly shows the Pb bound to aquatic humic substances (SAPP1) at different pH levels. The binding capacities of SAPP1 were 1.39E-2, 1.37E-2, and 1.44E-2 μM Pb/mg C for pH=3, 5, and 7, respectively.

Results of the AHA study were compared with the binding capacity of Cu with AHA according to an earlier report (Davis, 1993), found to be 2.25 μM Cu/mg C. Copper evidenced a stronger binding capacity than Pb. Comparison of SAPP1 data with those for Cu (Davis, 1993) showed that the Pb binding capacity of SAPP1 was less than the binding capacities of Cu with any other surface-water-derived humic substances. The same comparison for Pb could not be done due to a lack of data in the literature for Pb binding capacity with surface-water-derived humic substances. However, a study of metal-complexing capacity of dissolved organic carbon (DOC) from forest-soil leachates with metals suggested that the Pb binding capacity for soil-derived humic substances ranged from 1.00E-2 to 40.0E-2 μM Pb/mg C (Kuiters and Mulder, 1990).

Lead and its compounds tend to accumulate in soils and sediments where, due to their low solubility and relative freedom from microbial degradation, they may have a long residence time compared with other pollutants (Davies, 1990). The organic fraction of sediment was largely responsible for the observed fixation of the metal and Pb remaining near the soil/sediment surface (Alloway, 1990; Davies, 1990; Ton, 1990). Soil humus, especially high-molecular-weight humic acids, contributed most to the immobilization of Pb
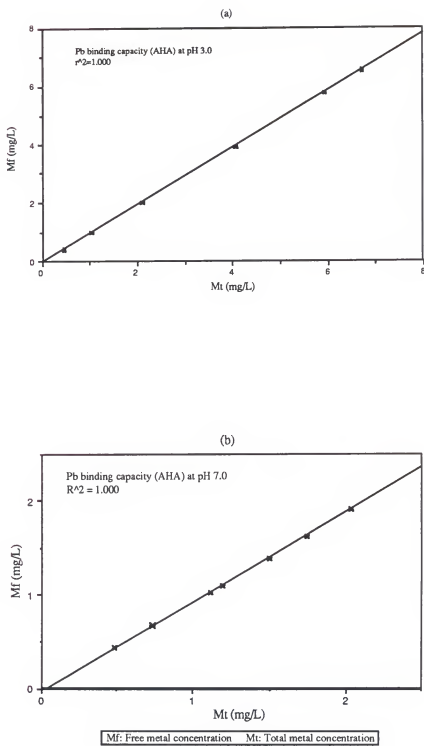
Figure 4-12. Lead binding capacities of Aldrich humic acid (AHA):
(a) pH 3.0 (b) pH 7.0.

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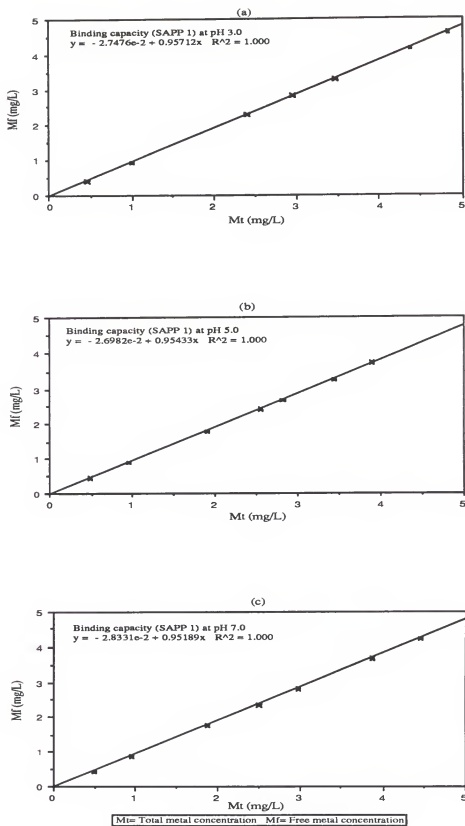
Figure 4-13. Lead binding capacities of SAPP 1 aquatic humic substances: (a) pH 3.0 (b) pH 5.0 (c) pH 7.0.

added to the soil with Pb being bound through coordinate binding by free electron pairs (Aiken et al., 1985; Davies, 1990; Snoeyink and Jenkins, 1980; Stumm and Morgan, 1981).

In heavily polluted soils, part of the Pb was present as a high-molecular-weight organo-Pb complex, and the proportion represented by this form was greater in soil of higher pH (Alloway, 1990). In contrast, some earlier studies suggested that the metal binding capacity values were not a strong function of pH for Cd^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} (Kuiters and Mulder, 1990; Saar and Weber, 1982; Truitt and Weber, 1981a; Weber, 1983).

4.3.2 Conditional Stability Constants for Organo-Pb Complexes

Scatchard plots for AHA are shown in Figure 4-14. Two slopes were obtained in each plot (section 3.4.2.2). The log conditional stability constants for Pb-AHA complexes were 5.71 and 4.78 for strong sites and weak sites, respectively. Similar patterns of Scatchard plots were obtained for SAPP1 at different pH values. These plots are shown in Figure 4-15 for pH 3, 5, and 7, respectively. The log conditional stability constants are listed in Table 4-11. These results indicate that the stability constants of aquatic humic substances increase with increasing pH.

In previous studies (section 2.4.4.1, Table 2-8) at pH 7, the log stability constants for AHA were 6.5 and 5.3 for strong and weak sites, respectively. Comparing the results from previous studies with those from the current study, slightly lower stability constants for AHA and water-derived fulvic acid is noticed.

A potential problem with the equilibrium dialysis technique is the permeation of humic substances through the hollow fiber cartridge. Similar phenomena were noted by Truitt and Weber (1981a). The leakage of humic substances across the membrane would lead to an underestimation of the Pb binding capacity and conditional stability constants as well. However, different methods for the determination of stability constants of metal

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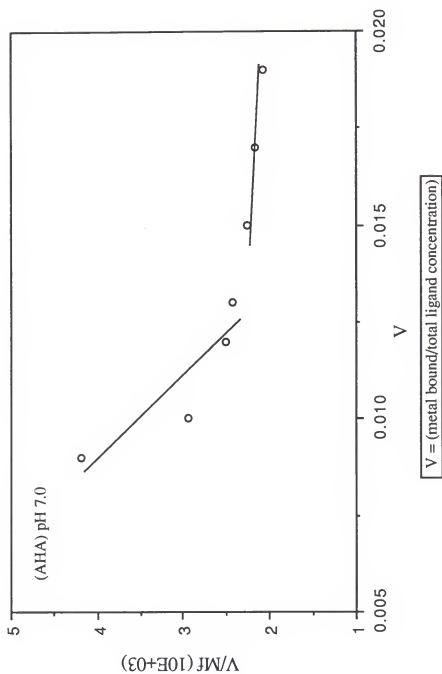
Figure 4-14. Scatchard plot for the stability constant of AHA at pH 7.0
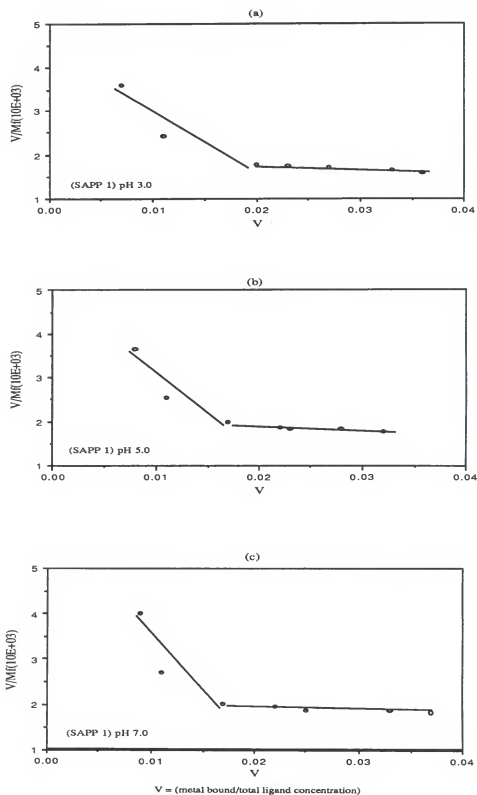
Figure 4-15. Scatchard plots for the stability constants of SAPP 1:
(a) pH 3.0 (b) pH 5.0 (c) pH 7.0.

Table 4-11. Conditional stability constant for complexes of aqueous humic substances
with Pb.

Complexes*	pH		Log stability constant ‡	
	3	S**	5.15	(r^2=0.534)
		W	4.71	(r^2=0.846)
Pb-AHA	7	S	5.71	(r^2=0.809)
		W	4.78	(r^2=0.981)
	3	S	5.10	(r^2=0.863)
		W	4.04	(r^2=0.982)
Pb-SAPP1	5	S	5.24	(r^2=0.864)
		W	4.10	(r^2=0.775)
	7	S	5.34	(r^2=0.801)
		W	3.92	(r^2=0.809)

* AHA-Aldrich humic acid.   SAPP1- surface water from Sapp site control pond (Figure 3-2).
** S-strong binding site.   W-weak binding site.
‡ see Figure 4-14 and Figure 4-15 of Scatchard plots for stability constants

complexes with humic and fulvic acids have made the comparison and interpretation of such data less meaningful (Stevenson, 1982). Moreover, the lowered accuracy and reproducibility of analytical measurements further increased the uncertainty for metal binding capacities and determinations of stability constants (Haworth et al., 1987).

By way of conclusion for the laboratory studies, the Pb binding capacity of humic substances as well as the conditional stability constants of organo-Pb complexes were related to pH. Under a reduced environment, an increase pH of the surface water enhances the formation of organo-Pb complexes. Consequently, the removal of organo-Pb complexes by mechanisms such as adsorption and precipitation at higher pH values further reduces the potential hazards of Pb pollution (Florence and Batley, 1980; Huang et al., 1977).

4.4 System Analysis -- Ecological-Economic Evaluation of Alternative Wetland Management

Several work plans were prepared in response to the U.S. EPA and FDER requests for a remedial investigation and feasibility study (RI/FS) at the Steel City Bay wetlands (CH$_2$M HILL, 1991; Mundrink, 1989; Watts, 1984). Remedial alternatives also were developed and proposed to the U.S. EPA and the FDER (Bechtel Environmental, Inc., 1991; Trnovsky et al., 1988). Two alternatives proposed in the aforementioned reports, and a restoration plan for the wetland ecosystem by replanting that is proposed herein, were evaluated using the ecological-economic method for wetland management. These alternatives include:

(A) Planting: to restore the wetland ecosystem by providing seedlings.

Such revegetation efforts would promote gross primary production (GPP) by the wetland ecosystem (Bradshaw, 1987). It would therefore enhance the biogeochemical processes for Pb (Nriagu, 1978a), and consequently reduce the toxicity effects of Pb in the wetland ecosystem. According to the sediment quality criteria (Bonnevie et al., 1992) and the contaminant cleanup criteria

(Trnovsky et al., 1988), a fence is needed for the Steel City Bay West wetland because average sediment concentrations are > 200 µg/g, to prevent human contact with contaminated sediments and protect human health.

(B) Land control: to restore the wetland ecosystem by natural processes.

In this case, no treatment is applied to the contaminated site. A fence for the Steel City Bay West wetland, to protect human health, is the only requirement. This is one of the alternatives being suggested to the FDER and EPA (Trnovsky et al., 1988). It is intended to serve as a baseline against which other alternatives can be measured.

(C) Sediment excavation: to remove and dispose of the contaminated sediment.

Removal of contaminated sediment for disposal in an off-site secure landfill is considered in this alternative. This action provides a high level of cleanup and prevents any further migration of contaminants. Cost for this alternative is estimated for the excavation action only; off-site disposal is not evaluated.

4.4.1. Emergy Analysis of Alternative Management

The system diagram (Figure 3-9) used for the emergy analysis portrays the ecosystem processes using symbols. The renewable resources including sunlight, wind, rain, and runin (surface water inflow) contribute to the ecological processes of wetland production. Lead is carried along with several of these processes and stored in compartments such as surface water, biomass, and sediment. Respiratory consumption by benthic organisms completes the biogeochemical cycle for the wetland ecosystem.

The outside, nonrenewable resources which were attracted to the system by wetland management can be considered as another energy input to the wetland ecosystem. By combining these two categories (natural inputs and outside resources), the function of the wetland ecosystem is altered. Some of the valuable wetland functions may be enhanced to some extent, but other functions may no longer be provided.

Table 4-12. Emergy evaluation of energy flows for alternative wetland management strategies.

Note	Item	Raw units	Transformity or Emergy / Unit	Solar Emergy (E15 sej)
	Energy Inflows (Renewable resources)			
1	Sunlight	1.07E+15 J/yr	1.00E+00 sej/J	1.1 sej
2	Wind	7.85E+10 J/yr	1.50E+03 sej/J	0.1 sej
3	Rain, chemical	9.10E+11 J/yr	1.82E+04 sej/J	16.6 sej
4	Runin	8.22E+11 J/yr	4.11E+04 sej/J	33.7 sej
	A. PLANTING:			
	Energy Inflows (Nonrenewable resources)			
5	Goods and services(Fence)	7.20E+04 $	2.00E+12 sej/$	144.0 sej
6	Goods and services(Seedlings)	3.01E+09 J	1.20E+05 sej/J	0.4 sej
7	Goods and services(O/M costs)	4.10E+03 $	2.00E+12 sej/$	8.2 sej
	Subtotal			152.6 sej
	Ecosystem Processes			
8	GPP	4.61E+13 J/yr	1.09E+03 sej/J	50.3 sej
	B. LAND CONTROL:			
	Energy Inflows (Nonrenewable resources)			
9	Goods and services (Fence)	7.20E+04 $	2.00E+12 sej/$	144.0 sej
	Ecosystem Processes			
10	GPP	1.43E+13 J/yr	1.09E+03 sej/J	15.6 sej
	C. SEDIMENT EXCAVATION:			
	Energy Inflows (Nonrenewable resources)			
11	Goods and services (Excavation)	1.53E+05 $	2.00E+12 sej/$	306.9 sej
	Energy Export			
12	Peat, sediment	9.50E+13 J	4.42E+03 sej/J	420.0 sej
	Ecosystem Processes			
13	GPP	1.43E+13 J/yr	1.09E+03 sej/J	15.6 sej
	Total emergy used/GNP (1990 US) =	2.00E+12 sej/$		(Odum et al., 1993)

Footnotes To Table 4-12.

1 SOLAR ENERGY:
Area (m^2) = 2.49E+05
Insolation (kcal/cm^2/yr) = 1.46E+03   (Odum et al., 1987)
Albedo (=30%) = 3.00E-01   (Odum et al., 1987)
Energy (J /yr) = (Area)*(ave insolation)*(1-albedo)*(1000cm^2/m^2)*(4186J/kcal)
= 1.07E+15

2 WIND, KINETIC ENERGY AT SURFACE :
Height (m) = 1.00E+03   (Odum et al., 1987)
Air density (kg/m^3) = 1.23E+00   (Odum et al., 1987)
Diffusion coefficient (m^2/s) = 2.25E+00   (Odum et al., 1987)
Wind gradient (1/s) = 1.90E-03   (Odum et al., 1987)
Surface wind (J /yr)= (Height)*(Density)*(Diffusion coefficient)*(Wind gradient)^2* (Area)*(1 J/s/watt)*(3.154E+07 s/y)
= 7.85E+10

3 RAIN, CHEMICAL POTENTIAL: Gibbs free energy (J/g) = 4.94
Rainfall (m /yr) = 1.48E+00   (U.S. Soil Conservation Service, 1979)
Evapotrans rate (m /yr) = 7.40E-01   (assume 50% ET rate)   (Ewel and Odum, 1986)
Energy of rain (J / yr)= (Area)*(Rainfall)*(ET rate)*(G)*(E+06 g/m^3)
= 9.10E+11

Table 4-12. Continued.

4 RUNIN: (Calculated from soil conservation service curve number)
      Annual runoff rate (m/yr) = 6.68E-01
           Energy (J / yr) = (Area)*(Annual runoff rate)*(1000 kg/m^3)*(4.94E+03 J/kg)
                         = 8.22E+11

5 GOOD AND SERVICES (FENCE):
               Length (ft) = 4.80E+03
               Unit price ($/ft) = 1.50E+01   (Bechtel, Inc., 1991)
    Human services embodied in equipment and fuel used ($) = (Length)*(Unit price)
                         = 7.20E+04

6 GOOD AND SERVICES (SEEDLINGS):
               Seedlings= 4.00E+03
               Biomass (g) = 4.00E+01
      Energy contents of biomass (J/g)= 1.88E+01   (Odum et al., 1987)
               Seedlings (J) = (Seedlings)*(biomass)*(Energy content of biomass)
                         = 3.01E+09

7 GOOD AND SERVICES (OPERATION & MAINTENANCE COSTS):
    Human services embodied in equipment and fuel = 4.10E+03   (Labors, misc.)

8 GROSS PRIMARY PRODUCTION:
       (GPP calculation based on the control forest wetland ecosystem) (Pritchard, 1992)
      Gross primary production = 1.85E+08   (J/m^2/yr)
            Energy (J)= (Area)*(GPP)
               = 4.61E+13

9 GOOD AND SERVICES (FENCE):
               Length (ft) = 4.80E+03
               Unit price ($/ft) = 1.50E+01   (Bechtel, Inc., 1991)
    Human services embodied in equipment and fuel used ($) = (length)*(unit price)
                        = 7.20E+04

10 GROSS PRIMARY PRODUCTION:
       (GPP calculation based on the damaged wetland ecosystem) (Pritchard, 1992)
      Gross primary production = 5.73E+07   (J/m^2/yr)
            Energy (J)= (Area)*(GPP)
               = 1.43E+13

11 GOODS AND SERVICES: Cost for excavation ($) = 8.67E+05   (BECHTEL, Inc., 1991)
              Total soil/sediment excavation (m^3) = 9.65E+05   (Trnovsky et al., 1988)
              Off-site sediment excavation (m^3) = 1.68E+04   (Trnovsky et al., 1988)
    Costs embodied in equipment and fuel used ($) = (Excavation costs)*(ratio of off-site excavation)
                         = 1.53E+05

12 PEAT (SEDIMENT):
           Peat (J) = (Total volume)*(Bulk density)*(Energy content of peat)
             = 9.50E+13   (Odum et al., 1987)

13 GROSS PRIMARY PRODUCTION:
       (GPP calculation based on the damaged wetland ecosystem) (Pritchard, 1992)
      Gross primary production = 5.73E+07   (J/m^2/yr)
            Energy (J)= (Area)*(GPP)
               = 1.43E+13

To characterize emergy values for the environmental work, an emergy evaluation table with an itemized list of energy flows from natural resources, imported resources, exports, and storages has been prepared. The emergy evaluation of energy flows for three alternative strategies of wetland management is shown in Table 4-12.

Energy inflows of renewable resources are estimated as a natural input received by a defined area. Thus, the natural input for the three alternatives is kept constant. Among the energy inflows, rain and runin are derived directly or indirectly from the energy of sun and wind. To avoid double counting of natural inputs, only the combination emergy of rain and runin (items 3 and 4, Table 4-12) is used to represent the emergy contribution to the wetland ecosystem, which has a value of 50.3E+15 sej (solar emjoules).

The different wetland management strategies also involve various goods and services. The emergy for each energy input is calculated by multiplying the energy of the material by its solar transformity. The transformity of human service, which usually is embodied in equipment and fuel used, can be obtained by dividing the total emergy used in the U.S. economy by the gross national product (GNP). The value is calculated as 2.0E+12 sej/$, according to U.S. economic figures for 1990.

Nonrenewable resources applied to the system for wetland restoration include fence construction, seedling supply, and operation and maintenance costs (items 5, 6, and 7, Table 4-12). Because of human health concerns due to the high elevated Pb concentrations of the sediment, a fence around Steel City Bay West is to be provided for protection. The emergy of seedlings and annual operations costs also are calculated according to their transformities. The summation of these nonrenewable resources is 152.6E+15 sej.

It is believed that replanting, the first alternative considered, will promote wetland production. After 20 years of revegetation, the Steel City Bay wetlands are assumed to gradually recover to normal conditions. Thus, the gross primary production (GPP) of this wetland ecosystem is based on the production of a normal forest wetland ecosystem. The

transformity of GPP in this study is obtained by dividing the total solar emergy of the wetland ecosystem by the energy of a forest wetland in primary production. The value is calculated to be 1091 sej/j (solar emjoules/joule). Thus, the emergy of a well-functioning wetland ecosystem (item 8, Table 4-12) is estimated at 50.3E+15 sej.

For the second alternative, the wetland itself is assumed to be preserved without any treatments. Concerns for elevated Pb concentrations in sediments to human health dictate adding a fence in this option (item 9 in Table 4-12). The emergy value for the fence is 144.0E+15 sej. Since Sapp Battery Service, Inc., has ceased operation, field measurements have revealed a slow recovery of wetland production (Pritchard, 1992). Because of this slow recovery, the GPP for the emergy calculations is based on field measurements for the damaged wetland ecosystem in 1991 (Pritchard, 1992), which are estimated at 1.43E+13 J/yr. The emergy value of the GPP for a damaged wetland ecosystem (item 10, Table 4-12) is then estimated as 15.6E+15 sej.

The third alternative, sediment excavation, is considered to be a highly effective alternative for cleaning up contamination; however, the high cost makes this option less acceptable (Trnovsky et al., 1988). Estimation of the cost of this operation (item 11, Table 4-12) is based on two earlier reports (Bechtel Environmental, Inc., 1991; Trnovsky et al., 1988). The ratio of the off-site contaminated sediment volume to total contaminated soil/sediment volume is 1.74E-02 (Trnovsky et al., 1988). By multiplying this ratio by the total cost for excavation, the costs embodied in equipment and fuel are obtained. The emergy for sediment excavation is estimated at 306.9E+15 sej.

The excavation action not only requires outside energy inputs but also exports the energy of the peat stored in the ecosystem. Therefore, the energy of sediment excavation (item 12, Table 4-12) is calculated by multiplying the mass of the excavated sediment by its energy content. The emergy value is then estimated to be 420.0E+15 sej.

Several assumptions are necessary for the GPP estimation of the sediment-excavation alternative. First, the excavation action may disturb the ecosystem or even

create a different ecosystem, such as development of a deep pond ecosystem. Second, the removal of sediment from the wetland area may reduce future nutrient supply for wetland production. Third, without proper management, the production recovery may cease or progress at only a slow rate (Bradshaw, 1987; Cairns, 1988). Thus, the GPP for this alternative (item 13, Table 4-12) is estimated as that for an ordinary pond system, and not very different from that for a damaged wetland ecosystem (Odum, personal communication).

4.4.2 Emergy Evaluation of Different Management Strategies

Based on the emergy analysis in section 4.4.1, an empower graph for wetland production is shown in Figure 4-16. The recovery rates from this graph provide a database for the emergy evaluation of the various wetland-management strategies. Recovery rates for the three alternatives are projected as 20 years, 62 years, or an indeterminable period from 1991, shown as (a), (b), and (c), respectively. Wetland production over time is calculated by estimating the associated areas; i.e., wetland empower (sej/yr) = wetland production (sej) / Time (yr).

The emergy evaluation of alternative management strategies with different recovery rates is summarized in Table 4-13. Emergy values for different works are listed for each alternative. Ecosystem processes, i.e., wetland production, and clean surface water being filtered and passed downstream are the major benefits provided to society by a wetland ecosystem. By subtracting the emergy input for wetland management from the benefit of natural work, a net benefit can be obtained for each specific wetland management strategy. For the purpose of comparison, a monetary unit (macroeconomic value, 1990 U.S.$) is used.

The net benefit emergy for wetland restoration by planting, alternative A, is 15.1E+17 sej and 57.4E+17 sej for the 20-year and 62-year recovery rates, respectively. Land control, alternative B, has a net benefit from 12.9E+17 sej to 55.1E+17 sej after 20
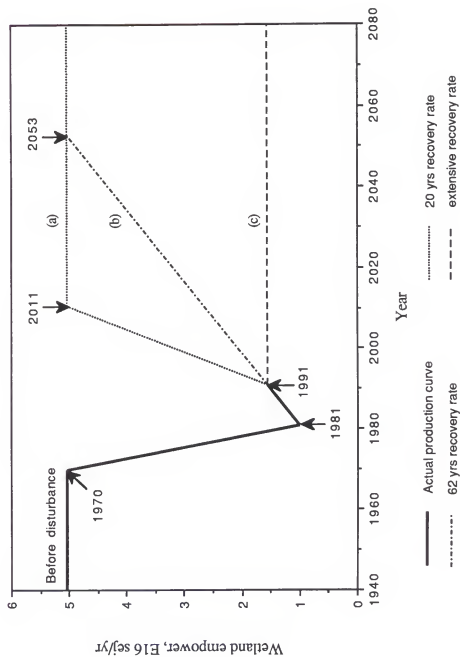
Figure 4-16. Empower graph of wetland production with three alternatives: (a) Planting (b) Land control (c) Sediment excavation.

Table 4-13. Continued.

5 WATER FILTERED AND PASSED DOWNSTREAM:
                 Same as Note 2.

6 MANAGEMENT COSTS:
      Datum from Table 4-12 (item 9) = 144.0 E15 sej/yr

7 ECOSYSTEM PROCESSES:
   Calculated from empower graph of wetland production (Figure 4-16)
                  Emergy (20 yrs) =   3.1 E17 sej
                  Emergy (62 yrs) =   9.7 E17 sej

8 WATER FILTERED AND PASSED DOWNSTREAM:
                 Same as Note 2.

9 PEAT-STORAGE LOSS:
          Calculated from Table 12 (Item 12) = 420.0 E15 sej/yr

10 MANAGEMENT COSTS:
      Datum from Table 4-12 (item 11) = 306.9 E15 sej/yr

11 EMERGY INVESTMENT RATIO:

$$\frac{\text{Emergy of management cost}}{\text{Emergy of environmental inputs}} \quad \text{(item 3+4, Table 4-12)}$$

12 NET EMERGY YIELD RATIO:

$$\frac{\text{Emergy of net benefit}}{\text{Emergy of management cost}}$$

years to 62 years of recovery. Due to the low productivity of pond systems, alternative C (sediment excavation) has the lowest benefit from natural input. The loss of sediment storage further reduces the net benefit for this option.

To apply the macroeconomic values to estimate the benefit to society after 20 years, $757,000, $643,000, and $296,000 are obtained for alternatives A, B, and C, respectively. The figures for 62 years are increased to $2,870,000, $2,760,000, and $1,680,000 for A, B, and C, respectively. Emergy investment ratio cab be obtained as:

$$\text{Emergy investment ratio} = \frac{\text{Emergy of management cost}}{\text{Emergy of environmental inputs}}$$

Results of emergy investment ratio are 3.03, 2.86, and 6.10 for alternatives A, B, and C, respectively. The net emergy yield ratio, which is the ratio of the emergy yield divided by the emergy used for processing, are obtained for alternatives A, B, and C as 9.92, 8.93, and 1.93, respectively.

The result of the net benefit calculations, i.e., macroeconomic values, suggest that alternative A is a better management strategy than the other two strategies for this impacted wetland ecosystem. Results of the emergy investment ratio calculations suggest that alternative C requires too much investment and cost from society, which would make this process economically uncompetitive. Results of net emergy yield ratio calculations were compared with some typical values of fuels and environmental products in an earlier report (Odum, 1993), ranging from 1.06 for palm oil to 12.0 for naturally grown rainforest wood. Alternative A evidenced a higher net emergy yield, i.e., 9.92, than for most environmental products, and was even greater than for oil production, i.e., 7.9. Comparison of restoration of the wetland by planting (alternative A) with reclamation of a phosphate mine by succession (phosphate reclamation) showed that the net emergy yield of alternative A was greater than the net emergy yield of phosphate reclamation (found to be 1.61, Brown, personal communication). Since a good public policy for a nation or a state is to pursue resources and/or invest in processes with the highest net emergy yield ratio

(Odum, 1993), the emergy evaluation practice in this study suggests that alternative A (planting) is the most appropriate management strategy for this impacted wetland ecosystem. Emergy evaluation proved to be a better way to value the nonmarketed goods and services which nature provides for our society.

CHAPTER 5
SUMMARY AND CONCLUSIONS

5.1 Summary

Results of the field, microcosm, and laboratory studies were used to support the decision-making process for wetland management. Analytical results of the field study indicated that the ecotoxicity of discharged wastes was reduced gradually by wetland biogeochemical processes. Only trace amounts of Pb still remained in the water column, and there was also a tendency for the pH of surface water to increase. Under constant flooded conditions, the potential of surface water recontamination was minimized. Elevated Pb concentrations in the surface water samples at site A and E were postulated to reflect the impact of high Pb concentrations in sediment deposition. Lead concentrations of the sediment revealed that the study area served as a sink for Pb, while increasing biomass and biodiversity observed in the field suggested progressive reduction in ecotoxicity effects for the wetland ecosystem.

Statistical analysis of the microcosm study data showed that there were no significant effects of pH and Pb contamination on the growth of seedlings. There was also no difference between species in response to ecotoxicity effects. However, the mean growth of seedlings suggested that the influence of Pb concentration was stronger than that of pH. In addition, a higher sensitivity of pond cypress was observed in response to Pb concentration stress. The same phenomena were observed in the field, where only the black gum community has slowly recovered to date.

The laboratory study showed that aquatic-derived humic substances (SAPP1) had less Pb binding capacity than the commercial humic acid (AHA). The binding capacity of Pb with SAPP1 was also less than the binding capacity of Cu with any other surface-water-

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derived humic substances. This Pb binding capacity was correlated to the pH of the aqueous environment. Under reduced conditions, the increase in pH of the water enhanced the binding of Pb to organic-rich sediments. The same phenomena were observed in the stability constant of organo-Pb complexes. As a result, controlling the surface water depth, and maintaining a reduced environment, is necessary for Pb retention in the system.

Advantages of a newly developed method of dialysis analysis were shown. The traditional method takes 48 hours to equilibrate; the method developed herein takes less than 6 hours. The on-line sampling of the new method allows easy access for sample and also provides of a contact-free sample collection, which reduces sample contamination. A wide range of pH and chemical compatibility of the hollow-fiber cartridge was shown for the new method. Low organic matter permeated through the hollow-fiber-cartridge during dialysis, due to the higher molecular-weight cutoff of fiber, was the major disadvantage of this method. A potential dynamic study is also available if selective-ion electrode probes could be used instead of frame AAS for metal concentration measurements.

Emergy analysis is an embodied energy analysis that provides common units of emergy for comparison of environmental and economic goods. This is done by summing the energy of one type of resource required directly or indirectly for its production. The emergy evaluation revealed that the restoration (replanting) of the wetland ecosystem was the most profitable alternative for society.

By replanting seedlings with no further disturbance of the functions of the wetland, an increase of biomass production should enhance the ecosystem processes. This was also suggested by the microcosm study, where all seedlings survive well under simulated current field conditions. Also, the woody species have a longer turnover rate than herbaceous aquatic plants, because the woody species can uptake and store Pb in tissue and further extend the recycling rate of Pb in the environment. The laboratory complexation study also showed that the organic-rich sediment acts as a sink for retention of Pb. Excavation of this sediment would not only destroy the chemical balance between surface

water and sediment, but also would remove the valuable organic storage function of the wetland.

According to the emergy evaluation, the macroeconomic value of wetland restoration, alternative A (planting), to society is estimated to be $757,000 and $2,870,000 for a 20- and 62-years recovering period, respectively, whereas excavation would be only $296,000 and $1,680,000. Further, there would be an additional cost for the excavation operation, estimated to be $150,000. Therefore, the ultimate resolution of the environmental contamination is most efficiently dependent on natural processes. Understanding the natural system and establishing a harmonious interface between humanity and nature should be the major goals of scientists, leading to land-use management philosophies which can allow a society to get the most benefit from nature's work and save other valuable resources.

5.2 Conclusions

The fate of Pb in a wetland ecosystem was investigated in this thesis research and a systematic approach to restoring the damaged wetland ecosystem was also demonstrated in field, microcosm, and laboratory studies.

The field study suggested that the wetland acted as filter to retain Pb. The biogeochemical cycle of Pb in the Steel City Bay wetland ecosystem showed that Pb was predominantly bound to sediments, and that only a trace amount of Pb remained in the water column, i.e., ≤ 0.01 mg/L.

Lead uptake and tolerance mechanisms of individual wetland species were demonstrated using bioconcentration factors (BCF). High values of BCF in the below-ground biomass suggested that sediment is likely the most important ambient environment for Pb enrichment of vegetation. Decreasing BCF values of *Eleocharis ba.*, *Eleocharis eq.*, and *Nymphaea od.* with Pb concentrations increased in the sediment, presumably

represented the decreased availability of sites to bind Pb as the Pb concentration increased. These may be used as a tolerance mechanism for such species.

The experimental microcosm results proved that there were no significant effects of pH and Pb contamination on the growth of seedlings under simulated current field conditions. Therefore, the devastation of the wetland community in the Steel City Bay can be postulated to be due to acute toxicity effects from lead containing acidic wastewater discharges from plant operation. Germination of seeds to regenerate new species was unlikely to happen due to the constantly flooded condition in the Steel City Bay wetlands. Artificial regeneration of wetland species would appear to be a proper approach to restore the impacted wetland ecosystem.

Organically bound Pb was the most abundant chemical form of Pb in sediments, so the stability of Pb associated with organic substances is very important when characterizing potential hazards of Pb to the wetland ecosystem. Results of Pb binding capacity and conditional stability constants of organo-Pb complexes were related to pH. In the laboratory, under a reduced environment (absence of dissolved oxygen), as the pH of surface water was increased, then was a slight increase of Pb binding capacities and in the logs of the conditional stability constants.

Three alternatives for wetland management were evaluated using a systems analysis ecological-economic evaluation method. Results of net benefit calculations (macroeconomic value), emergy investment ratio, and net emergy yield ratio suggested that the alternative of planting to restore the wetland ecosystem (alternative A) is the most appropriate management strategy for this wetland ecosystem. This alternative was also supported by the results of the field and microcosm studies. Although field measurements showed low productivity in the wetland ecosystem, the increasing biodiversity and biomass over time indicated gradual recovery of this wetland ecosystem. Thus, planting seedlings to regenerate the wetland community at a metal-contaminated site is a practical approach for ecological restoration.

APPENDICES

APPENDIX A

DIURNAL OXYGEN MEASUREMENTS IN THE STEEL CITY BAY WETLANDS,
JACKSON COUNTY, FLORIDA.

Time*\Sampling site	B	C	F	D	G
	DO ppm				
23:00 - 2:00	0.35	0.55	1.20	0.65	0.18
2:00 - 5:00	-	-	-	0.40	-
5:00 - 8:00	0.23	0.28	0.78	0.23	0.23
8:00 - 11:00	0.15	0.23	2.25	0.68	0.60
11:00 - 14:00	0.15	0.25	3.13	2.13	-
14:00 - 17:00	0.15	0.88	3.38	2.63	3.13
17:00 - 20: 00	0.78	1.80	3.20	2.00	2.75
20:00 - 23:00	0.50	1.23	2.05	1.00	0.48

*See Figure 3-2 for locations of the sampling sites.
Data cited from Pritchard (1992)   - indicates no data available

APPENDIX B

WATER CHEMISTRY AND ASSOCIATED LEAD CONCENTRATIONS OF
SURFACE WATER, SEDIMENT, AND VEGETATION SAMPLES

Water chemistry -- pH and electrical conductivity

pH in surface water

Site/Date	Apr-89	Feb-90	Aug-90	Sep-90	Jun-91	Jan-92	May-92	AVG	SD	MAX	MIN
A	3.4	-	-	-	-	3.6	3.5	3.7	0.37	4.2	3.4
A0	-	3.9	-	-	-	-	3.9	3.9	-	3.9	3.9
B	3.6	-	4.1	3.8	4.2	4.9	4.1	4.1	0.42	4.9	3.6
C	3.8	-	3.7	4.0	4.2	4.8	4.0	4.1	0.37	4.8	3.7
D	4.5	-	4.2	-	4.3	5.0	4.6	4.5	0.32	5.0	4.2
E	-	3.9	-	-	4.8	5.2	4.6	4.6	0.56	5.2	3.9
F	4.5	-	3.8	-	4.3	5.5	4.4	4.5	0.62	5.5	3.8
G	3.9	-	4.6	-	4.4	4.9	4.6	4.5	0.39	4.9	3.9
H	-	-	5.0	-	5.0	5.8	4.6	5.1	0.50	5.8	4.6
OF1	-	-	-	4.0	4.2	5.9	5.0	4.8	0.87	5.9	4.0
OF2	-	-	-	3.8	4.5	4.6	4.5	4.3	0.36	4.6	3.8
FC	-	-	-	-	4.9	7.0	5.0	5.6	1.20	7.0	4.9

Electrical conductivity in surface water (S/cm)

Site/Date	Apr-89	Feb-90	Aug-90	Sep-90	Jun-91	Jan-92	May-92	AVG	SD	MAX	MIN
A	322.0	-	-	-	42.3	180.0	139.7	171.0	116.08	322.0	42.3
A0	-	-	-	-	-	-	61	61.0	-	61.0	61.0
B	106.0	-	38.3	64.9	34.0	49.6	40.5	55.5	27.05	106.0	34.0
C	76.4	-	46.9	44.6	27.0	37.0	36	44.6	17.06	76.4	27.0
D	30.8	-	28.6	-	23.2	28.0	30.7	28.3	3.09	30.8	23.2
E	-	-	-	-	29.2	65.2	43.4	45.9	18.13	65.2	29.2
F	47.4	-	61.3	-	30.5	48.0	32	43.8	12.76	61.3	30.5
G	76.5	-	100.1	-	27.0	46.6	28	55.6	31.92	100.1	27.0
H	-	-	72.7	-	31.6	45.0	42	47.8	17.55	72.7	31.6
OF1	-	-	-	39.7	25.0	32.0	34	32.7	6.05	39.7	25.0
OF2	-	-	-	56.8	25.5	67.4	26.8	44.1	21.21	67.4	25.5
FC	-	-	-	-	29.5	46.7	40	38.7	8.67	46.7	29.5

Water chemistry -- water depth, dissolved oxygen, and temperature

Depth in surface water (in)

Site\Date	Apr-89	Feb-90	Aug-90	Sep-90	Jun-91	Jan-92	May-92	AVG(cm)	SD	MAX	MIN
A	20	-	-	-	18	8	13.5	37.8	13.5	50.8	20.3
A0	-	-	-	-	-	-	24	61.0	-	61.0	61.0
B	20	12	-	-	36	27	10	53.3	27.4	91.4	25.4
C	30	-	-	-	40	28	14.5	71.4	26.6	101.6	36.8
D	40	-	-	-	52	32	20	91.1	33.7	130.8	50.8
E	-	16	-	-	27	12	5.5	38.1	22.4	67.3	14.0
F	18	-	-	-	32	22	14	54.6	19.6	81.3	35.6
G	16	10	-	-	29	30	28	57.2	22.8	76.2	25.4
H	-	-	-	-	24	20	9	44.7	19.5	60.3	22.9
OF1	-	12	-	-	29	10	8	37.1	23.9	72.4	20.3
OF2	-	-	-	-	21	17	12.5	42.5	10.5	52.7	31.8
FC	-	-	-	-	35	17	16	57.6	27.2	88.9	40.6

Temperature range

Jan. (7.5°C ~10°C)
April (29°C ~ 33°C)
May (21°C ~ 31°C)
June (22.5°C ~ 28°C)

DO in surface water (mg O/L)

Site\Date	Jun-91
A	2.00
A0	-
B	0.75
C	1.25
D	0.90
E	0.90
F	2.25
G	2.50
H	2.25
OF1	1.50
OF2	1.00
FC	2.00
FC	3.00

Lead concentrations -- surface water, sediment, and animal samples

Pb in surface water (mg/L)									
Site\ Date	Apr-89	Feb-90	Aug-90	Jan-92	May-92	AVG	SD	MAX	MIN
A	0.28	-	0.01	0.14	0.09	0.13	0.11	0.3	0.0
A0	-	-	-	<0.01	0.01	0.01	0.01	0.0	0.0
B	0.03	0.01	0.02	0.01	0.01	0.02	0.01	0.0	0.0
C	<0.01	0.01	<0.01	<0.01	0.01	0.01	0.00	0.0	0.0
D	<0.01	<0.01	0.01	<0.01	<0.01	0.01	0.00	0.0	0.0
E	-	-	0.01	0.20	0.06	0.09	0.10	0.2	0.0
F	0.01	0.01	<0.01	0.01	<0.01	0.01	0.00	0.0	0.0
G	<0.01	0.01	<0.01	<0.01	<0.01	0.01	0.00	0.0	0.0
H	-	0.03	0.01	<0.01	<0.01	0.02	0.01	0.0	0.0
OF1	-	-	<0.01	<0.01	<0.01	<0.01	0.00	0.0	0.0
OF2	-	-	<0.01	<0.01	<0.01	<0.01	0.00	0.0	0.0
PC	-	-	<0.01	<0.01	<0.01	<0.01	0.00	0.0	0.0

Pb in sediment (µg/g)									
Site\ Date	Apr-89	Feb-90	Aug-90	Jan-92	May-92	AVG	SD	MAX	MIN
A	385.7	-	393.9	27.7	23.4	207.7	210.3	393.9	23.4
A0	-	-	-	-	36.2	36.2	0.0	36.2	36.2
B	210.9	-	763.7	113.0	74.5	290.5	320.6	763.7	74.5
C	234.2	-	278.9	23.5	48.8	146.3	129.0	278.9	23.5
D	59.4	-	303.6	10.6	49.2	105.7	133.6	303.6	10.6
E	-	477.8	-	342.1	512.0	444.0	89.8	512.0	342.1
F	88.5	-	472.2	99.9	125.7	196.6	184.4	472.2	88.5
G	94.3	-	99.6	87.4	62.0	85.8	16.7	99.6	62.0
H	-	-	215.7	36.3	112.9	121.6	90.0	215.7	36.3
OF1	-	133.3	-	23.5	10.6	55.8	67.4	133.3	10.6
OF2	-	-	-	10.6	10.6	10.6	0.1	10.6	10.6
PC	-	-	-	23.3	23.4	23.4	0.0	23.4	23.3

Pb in Animals (µg/g)									
Site\ Date	Oct-89								
Beaver-L	13.3								
F-Cen	66.7		F -sampling site						
F-Cen	50.0								
G-ESOX	16.7		G -sampling site						
Beaver-L	Castor fiber		(liver)						
Cen	Centarchus								
ESOX	Esox lucius								

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Lead concentrations -- vegetation samples

Pb in vegetation (µg/g)

Site\Date	Apr-89		Feb-90		Aug-90		Jan-92		May-92
A-EL sp.	487.5	E-JL	850.0	A-EL eq.AG	61.2	A-EL eq.AG(N)	35.9	AI-AG	35.8
A-TAa	112.5	E-JR	1716.7	A-EL eq.BG	736.7	A-EL eq.BG(N)	86.0	AI-BG	125.6
A-TAb	37.5	F-TAc	<10.0	A-EL sp.AG	235.7	A-EL eq.(O)	789.2	AII-AG	10.5
B-TAa	56.3			A-EL sp.BG	620.2	A-EL sp.AG	241.3	AII-BG	151.3
B-TAb	12.5			B1	23.3	A-EL sp.BG	600.1	AIII-AG	10.6
B-TAc	<5.0			B2	10.6	B1(N)	36.0	AIII-BG	959.0
B-NSc	12.5			B3	61.6	B1	73.7	AIV-AG	164.6
B1&2	75.0			C1	23.0	B2	74.5	AIV-BG	762.9
B3	62.5			C2	10.5	B3	23.5	AV-AG	87.6
C-TAa	75.0			C3	10.6	C1	23.5	AV-BG	444.1
C-TAb	175.0			D1	10.6	C2	23.4	AVI-AG	267.5
C-TAc	<5.0			D2	10.5	C3	10.5	AVI-BG	585.0
C1&2	12.5			D3	10.4	D1	10.5	AVII-AG	<10.0
C3	12.5			F1	48.7	D2	10.6	AVII-BG	176.5
D-TAa	<5.0			F2	49.0	D3	10.5	A1	369.5
D-TAb	12.5			F3	23.2	E1	18.4	A2	341.8
D-TAc	<5.0			G1	10.6	E2	252.6	A3	23.3
D-NSa	18.8			G2	23.1	E3	183.5	A01	74.7
D-NSb	<5.0			G3	10.5	E-JL	201.4	A02	61.7
D1&2	12.5					E-JR	1241.2	A03	<10.0
D3	-					E-JL(OLD)	418.6	A04	10.6
F-TAa	<5.0					F1	10.6	B1	23.5
F-TAb	<5.0					F2	10.6	B2	10.6
F-TAc	<5.0					F3	10.6	B3	10.5
F1&2	12.5					G1	36.1	B4	<10.0
F3	50.0					G2	23.4	C1	10.6
F-ALG	150.0					G3	10.6	C2	10.6
G-TAa	12.5					OF1-1	23.5	D1	10.6
G-TAb	<5.0					OF1-2	10.6	D2	10.6
G-TAc	-					OF1-3	10.6	D3	<10.0
G-NSa	25.0					PC1	10.6	E1	203.1
G-NSb	37.5					PC2	10.5	E2	151.3
G-NSc	12.5					PC3	10.5	E3	317.6
								EJL	395.1
								EJR	2068.2
								F1	36.1
								F2	10.5
								F3	10.6
								F4	<10.0
								G1	10.6
								G2	<10.0
								G3	10.6
								H1	10.6
								H2	10.6
								H3	<10.0
								OF1-1	10.6
								OF1-2	10.6
								OF1-3	10.6
								OF1-ALG	35.9
								OF2-1	<10.0
								OF2-2	10.6
								OF2-3	<10.0
								P1	<10.0
								P2	<10.0
								P3	<10.0
								P4	<10.0

Symbols:			
TA-Taxodium ascendens		a-Bark	(N)-NEW
NS-Nyssa sylvatica		b-Stem	(O)-OLD
		c-Leaves	
A[B...]X-Nymphaea odorate		1-Leaves	
		2-Stem	
		3-Root	
		4-Flower	
J-Juncus		L-Leaves	
		R-Root	
EL sp.-Eleocharis sp.		AG-Aboveground biomass	
EL eq.-Eleocharis eq.		BG-Belowground biomass	
ALG-Algae			
AI-Amphicarpum muhlenbergianum			
AII-Eleocharis episetoides			
AIII-Hypericum fasciculatum			
AIV-Eleocharis sp.			
AV-Ludwigia sp.			
AVI-Xyris sp.			
AVII-Cyperus sp.			

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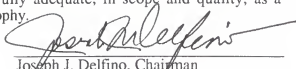
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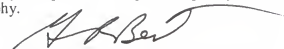
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